

Metorex

X-MET 880 OPERATING INSTRUCTIONS MANUAL

VERSION 1.0.1

3885 404-4VE

X-MET 880 ALLOY ANALYZER START-UP AND OPERATING PROCEDURE

1. Connect Probe to Electronic Unit, switch-on power and allow 15 minute warm-up. (Probe trigger should be released and prompt ">_" sign should be in lower left corner of display).

2. If Model number in lower right corner of display is not set to "1" then press "MODEL" key, enter a "1" and press the "CONT/YES" key to accept the entry. The lower right hand corner of the display should change to "1" (Model 1) and the upper right hand corner should display a "5s" (Measuring Time in sec).

3. Measure each of the check samples provided with the X-MET, by placing each in turn on the probe, then pull and hold the trigger open for the preset time of 5 seconds. (ALWAYS BE SURE THE SAMPLE IS COMPLETELY COVERING THE APERTURE!) After each measurement the X-MET will "beep" three times followed by a display of the alloy ID as well as a label indicating "GOOD MATCH", "POSSIBLE MATCH", OR "NO GOOD MATCH FOUND" followed by a match number. The match number is lower for a better match. (Note that the match number will vary somewhat for repeat measurements. This is normal and is not a cause for concern.)

4. If alloy composition is desired, switch to model #2 and measure each check sample for the preset time of 30 seconds. Compare the assays displayed with the expected readings for the elements in the check samples as noted on the data sheet for the check samples. The readings should be within +/-3 sigma (3X) of the standard deviation values calculated and displayed when the "STD" command is invoked (on-line standard deviation calculation).

4a. Should any readings be outside the 3 sigma values, use the "STA" (standardize) command and measure the check sample in question for the 200 second default time. After the 200 second re-standardization the X-MET will display the "RD's" (relative deviations) for each element, making appropriate corrections for any element that is outside the 3 sigma tolerance band. NOTE: by pressing the "RECALC" (recalculate) key, the X-MET will display the measured results which should now be all within acceptable limits (+/-3 sigma).

5. When all check samples read correctly, proceed with measurement of unknowns by selecting either "MODEL" #1 for ID or #2 for ASSAY operations.

6. Repeat the check sample measurement procedure daily to verify proper operation before beginning sample measurements.

NOTES

1. When using either MODEL 1 or 2 the X-MET electronically selects the correct alloy base material/calibration model (Automatic Model Switching) from all the available pre-calibrated models. (See summary calibration form.) Should your alloy be of a base material type or a specific grade, that is not already included in the standard calibrations, the X-MET will display "NO GOOD MATCH FOUND" and it will be necessary for you to enter your alloy into the X-MET ID reference library using the "ADD" command, or to create a new assay model. See detailed operating instructions for a full description of these procedures.

2. Should you desire to exit the automatic model switching program, simply change to the desired model, other than #1 or #2, and press the "END/NO" key. This allows X-MET to remain in the selected model.

CAUTIONS

1. NEVER POINT THE PROBE AT YOURSELF OR CO-WORKERS AND PULL THE TRIGGER.

2. NEVER PULL THE TRIGGER WITHOUT A SAMPLE OVER THE MEASURING APERTURE.

3. NEVER ATTEMPT TO OPERATE THE PROBE IF THERE IS A FAILURE IN THE PROBE SHUTTER (X-RAY SHIELDING) MECHANISM.

4. ALLOW THE GAIN CONTROL TO OPERATE AT LEAST EVERY HOUR OR WHEN A TEMPERATURE CHANGE OF GREATER THAN A FEW DEGREES FAHRENHEIT OCCURS.

5. NEVER ATTEMPT TO TAKE SAMPLE MEASUREMENTS WITH AN ERROR MESSAGE IN THE DISPLAY.

6. NEVER ATTEMPT TO UNPLUG THE PROBE BY PULLING ON THE WIRE.

7. DO NOT ATTEMPT TO ROTATE THE HANDLE WITHOUT FIRST PUSHING IN THE HANDLE RELEASE BUTTONS LOCATED ON EITHER SIDE OF THE HANDLE.

X-MET 880 MANUALS

3885 404-4VE

1

**OPERATING INSTRUCTIONS X-MET 880
ANALYZER VER. 1.0.1**

3881 432-4VE

2

**SOFTWARE GUIDE FOR X-MET 880
VER. 2.0**

3885 399-4VE

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1. GENERAL INFORMATION

1.1 Introduction and the use of the manual

This operating manual for the X-MET 880 X-ray fluorescence analyzer serves as a guide for preparing, operating and maintaining the instrument. The manual has been divided into sections as follows:

2) The X-ray fluorescence: concept and application

This part serves as an introduction to the field of technology applied, also covering the main physical aspects of the measurements.

3) The principal components of the analyzer

This describes the main components of the analyzer and their operation.

4) Pre-operating instructions

This section deals with the procedures preceding the use and calibration of the instrument. Calibration sample preparation is also covered in this section.

5) Calibration of the analyzer

This section is actually divided into two parts. The first part, **THE INSTRUMENT CALIBRATION**, details the procedures necessary to prepare an instrument for the sample calibration.

The second part, **THE SAMPLE CALIBRATION**, describes the setting of a calibration model (program). There are two kinds of models: assay models and identification models.

6) Measurements

This section covers the measurement operations and the associated commands.

7) Optional equipment

This section deals with optional devices that can be used to facilitate the X-MET operations. All the standard operations and procedures can, however, be performed without this equipment.

8) Maintenance

This gives insight into routine maintenance tasks associated with X-MET and its accessories. In case of actual malfunction, contact a representative of Metorex, Inc.

9) Troubleshooting

This section gives assistance in solving possible problem situations.

10) Appendices

Contain additional information on calibrations, special features, useful hints, principles etc.

The best way to learn the use of the instrument is to read part by part the manual through, and to play with the instrument. Testing the commands with e.g. the default 15 s measurement time is very recommendable. Chapter 2 contains the necessary theory, and chapters 4 and 5 contain the practical information.

1.2 Warnings

D A N G E R ! NUCLEAR RADIATION !

The probe contains a nuclear radiation source. The probe must not be opened except by authorized personnel.

If the screws of the probe are opened, the probe is rendered unsafe!

D A N G E R ! CORROSION OF BERYLLIUM

Beryllium compounds are toxic. Beryllium windows are used in proportional counters and low-energy radiation sources.

If exposed to moisture, beryllium easily corrodes, resulting in toxic compounds. Moisture may also destroy the proportional counter. However, this will not cause a radiation hazard. Corrosion of the source window may produce a radiation hazard. Thus, if moisture (liquid) enters the probe, it should be noted and a leak test carried out to the source. In such cases always notify a representative of Metorex Inc.

WARNING !

Calibration and the use of a probe closer than 1 meter to a cathode ray tube, a TV set or an equivalent strong source of radiation may result in erroneous measurement results.

1.3 Specifications

OPERATING PRINCIPLE

Energy-dispersive XRF with a 256 microchannel multichannel analyzer (MCA). Sample irradiation with a sealed low activity radioactive source at 5.9, 14.2, 22.1 or 59.8 keV. High resolution proportional counter detector (Ne- or Ar filling), resolution 13 % at 5.9 keV. 16/32 bit MC 68000 main processor, module type electronic. Probe design approved by all major radiation protection officials, acquired dose at 10 cm distance max. 1/3 of allowable weekly dose on hands (40 h exposure), with strongest source (Cm-244, 100 mCi).

OPERATING CONDITIONS

Ambient temperature:

* Electronic unit XAES

Operation 0°C to +60°C

Storage -20°C to +60°C

Charging 0°C to +60°C

* Surface probes SAPS and DOPS

Operation 0°C to +60°C

Storage -40°C to +85°C

* Probes HEPS, LEPS and SLPS

Operation 0°C to +60°C

Storage -40°C to +85°C

Notice the following:

- * A special low-temperature version of the instrument can safely be used down to -25°C.
- * Calibration and measurements should preferably take place at the same temperature. After a considerable change in temperature a stabilization interval of about 30 min./20°C should be allowed, with the instrument in the ON position and the probe connected (in gain control position) for the last 10 min.
- * Charger unit must be used only indoors in dry conditions.
- * The freezing temperature of the lead battery depends on the charge level of the battery. For a fully charged battery, freezing temperature is approx. -80°C; for a discharged battery respectively -10°C. The battery shouldn't be allowed to freeze, even though the battery will restore most of its charging capacity after thawing.

Charging voltage and power:

- * 115V \pm 20% / 50 to 60 Hz / 20VA maximum
- * 230V \pm 20% / 50 to 60 Hz / 20VA maximum
- * Fuse 0.5 A slow, glass tube (in charger)

For changing charging voltage, or fuse, see section 3.3 and 3.11

Charging and operation times:

- * Charging time in OFF-state: max. no limit
 min. 14 hours
- * Charging time in ON-state: max. no limit
 min. 30 hours
- * Operating time on fully
 charged batteries: max. 10 hours
 (dependent on ambient temperature)

Storage times for fully charged batteries:

= recommended maximum time a battery is stored in the given temperature. After this recharging has to be performed..

0°C to 25°C	2 years
50°C	6 months
70°C	1 month

Notice the following:

In storage the electronic unit should have as fully charged batteries as possible. Also spare batteries should be stored fully charged whenever possible. Otherwise they will lose their charging capacity in course of time.

Shock resistance:

Although the instrument is made to resist shocks occurring in normal field use, transport and operation, the instrument must not be dropped or left in exceptional conditions which might damage its sensitive components, especially the probes.

Guaranteed specifications for mechanical shock resistance:

- * Vibration 2 g, 10 Hz to 150 Hz
- * Bump 25 g

NOTE!

Even smaller vibrations may lead to inaccuracies in results if the probe is influenced, especially during a measurement.
After a shock let the instrument do gain control for at least 5 minutes uninterrupted.

Air pressure:

- * 30 to 200 kPa (4.35 to 29 lb/in²), (1/3 to 2 atm)

NOTE!

When using the light element detector (probe LEPS or SLPS), calibrations made at one altitude may not be valid for another altitude. This is because of changes in air density (effective air path length).

Humidity:

The electronic unit and the surface probes SAPS and DOPS are splash water proof (IP55). However, they should not be exposed to rain. Use the special X-MET bag (an accessory).

Probes HEPS, LEPS and SLPS are designed for indoor use only.

The silicagel bags in the probes and the electronic unit are used to remove possible moisture. They must be replaced or regenerated if their color turns pink - in outdoor use at least once a year (contact your Metorex Inc. representative).

1.4 Local regulations concerning the use of radioactive products

Preparations should be made with respect to the radiation legislation and regulations valid in each country.

In most countries, a special licence is needed for the possession of radioactive sources.

Contact your local radiation authorities and your representative of Metorex Inc.

WARNING !

Only persons with a formal training and a legal licence are allowed to open probes and handle radioactive sources.

2. X-RAY FLUORESCENCE: CONCEPT AND APPLICATION

2.1 Introduction

This section briefly describes the energy dispersive X-ray fluorescence method (EDXRF) as applied in the X-MET 880. The basic idea of a measurement is that a wide energy range of the X-ray spectrum is under observance simultaneously.

First, some concepts that are used in the XRF (and X-MET) technology:

- * Background is the noise, or unwanted signal, in the spectrum. In the X-MET, most of the noise originates from the backscatter. The background is subtracted on the basis of the BS, or backscatter, sample data.
- * Backscatter is the radiation of the source reflected from the sample, i.e. of the same energy. Another type of backscatter is Compton backscatter, which occurs when primary X-ray photons undergo an unelastic collision with sample electrons, and are reflected back with a smaller energy (especially notable with Cm-244 and Am-241 sources).
- * Characteristic lines are energies (wavelengths) at which elements radiate X-rays, when irradiated with a higher energy radiation.
- * Dependent variables are the elements which are desired to be analysed (analytes).
- * Element windows are sections of the spectrum on the energy scale, where received pulses are calculated as coming from a specific element. In the X-MET, windows are opened with PUR command.
- * Escape peaks are "shadow" peaks in the spectrum with a lower energy than a major peak has. Their origin is in the detector filling gas (Ar or Ne), which gives its characteristic radiation.
- * FWHM stands for full width at half maximum height. It is the width of an element peak in the spectrum at 50 % height, expressed either in energy units or in microchannels.
- * Gain control is the automatic compensation for electronic drift, changes in temperature and pressure etc. in the X-MET. It starts to operate when the probe is initialized.
- * Heavy elements = elements from Cr upwards in the periodical system.
- * Independent variables are measured intensities of elements, or combinations thereof, which are used to explain the concentration of an element (through the measured intensity of that and other elements).
- * Interfering element = an element which can either absorb or enhance the analyte's fluorescent radiation; also, a neighbouring element.
- * Matrix is the substance where the analyte is embedded, more often "all the other elements except the analyte".
- * Microchannel: the spectrum is divided into 256 microchannels.
- * Normalization is the compensation for a decrease in the radiation output of a source.
- * Resolution is a value describing the ability of the instrument/detector to separate two close peaks.
- * Spectrum is the measured energy (microchannel) vs. intensity graph, or equivalent data.

2.2 The excited X-ray spectrum

Radiation from the source strikes the sample and excites the sample atoms, by kicking out an electron from them. With the transition of the atom into a stable state, fluorescent (characteristic) X-rays appear. Also, scattered X-rays are "reflected" from the sample. A simplified X-ray spectrum is shown schematically in figure 2.1, see also figure 3.1.

2.3 Characteristic X-rays

Fluorescent X-rays have sharply defined peak energies characteristic of the elements excited. This is why qualitative analysis becomes possible.

The unit of the X-ray photon energy is 1 keV (kilo electron volt). Using the radiation energy instead of wavelength or frequency is traditional in X-ray technology. A photon of energy 12.39 keV has a wavelength of ca. 1 Angstrom unit (1×10^{-10} m).

Figure 2.1 shows the characteristic lines of the elements Fe, Cu and Zn and scattered X-rays. The dotted curves indicate how the detection process spreads the lines as the X-ray quanta are converted into electrical pulses. See also fig. 3.1 for the atomic level explanation of the X-ray fluorescence phenomenon.

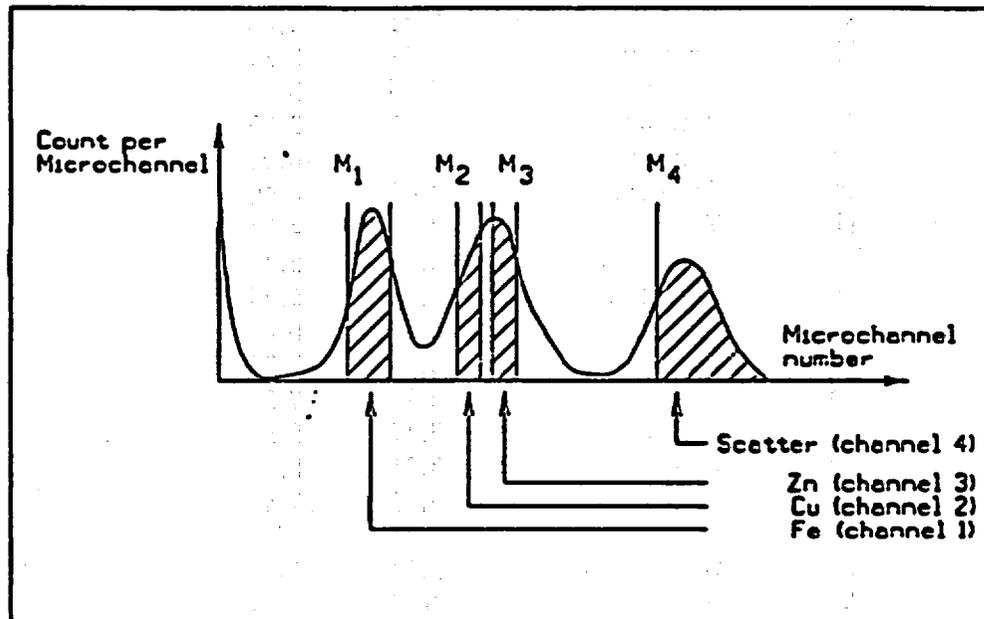


Figure 2.1 Characteristic spectral lines and the spreading of detected pulses.

Notice that the K lines for a given element are the most energetic lines and are generally the lines to be employed for analysis (the K_{α} line being preferred to the K_{β} line). If the K lines are excited, the L and M lines of the same element will also appear, but being of a much lower energy they can usually be neglected. For heavy elements (such as Ce, $Z=58$, to U, $Z=92$) the L lines are used for the X-MET analysis. Notice that the L_{α} and L_{β} lines have almost equal intensities and the choice of either one depends on what interfering lines (elements) are present. A source just energetic enough to excite the L lines will not excite the K lines of the same element.

Tables A and B contain the energies and approximate intensity ratios of the characteristic X-ray lines for all the elements that can be analyzed by using the X-MET analyzer. An X-ray source can excite characteristic X-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element (i.e. K absorption edge, L absorption edge, M absorption edge). The absorption edge energy is somewhat greater than the corresponding line energy. (Actually the K absorption edge energy is approximately the sum of the K, L and M line energies of an element, and the L absorption edge energy is approx. the sum of the L and M line energies of the element etc.).

Table A. Energies of certain K and L lines in keV.

Atomic number	Symbol	Element	Intensity ratio		Intensity ratio		
			7 : 1	9 : 6 : 1	7 : 6 : 1	9 : 6 : 1	7 : 6 : 1
			K _α	K _β	L _α	L _β	L _γ
12	Mg	Magnesium	(1.25)	(1.30)			
13	Al	Aluminum	1.49	1.55			
14	Si	Silicon	1.74	1.83			
15	P	Phosphorus	2.02	2.14			
16	S	Sulphur	2.31	2.46			
17	Cl	Chlorine	2.62	2.82			
18	Ar	Argon	2.96	3.19			
19	K	Potassium	3.31	3.59			
20	Ca	Calcium	3.69	4.01			
21	Sc	Scandium	4.09	4.46			
22	Ti	Titanium	4.51	4.93			
23	V	Vanadium	4.95	5.43			
24	Cr	Chromium	5.41	5.95			
25	Mn	Manganese	5.89	6.49			
26	Fe	Iron	6.40	7.06			
27	Co	Cobalt	6.92	7.65			
28	Ni	Nickel	7.47	8.30			
29	Cu	Copper	8.04	8.94			
30	Zn	Zinc	8.63	9.61			
31	Ga	Gallium	9.24	10.3			
32	Ge	Germanium	9.87	11.0			
33	As	Arsenic	10.5	11.8			
34	Se	Selenium	11.2	12.6	(1.38)	(1.42)	
35	Br	Bromine	11.9	13.4	1.48	1.53	
36	Kr	Krypton	12.6	14.2	1.59	1.64	
37	Rb	Rubidium	13.4	15.1	1.69	1.75	
38	Sr	Strontium	14.1	16.0	1.81	1.87	
39	Y	Yttrium	14.9	16.9	1.92	2.00	
40	Zr	Zirconium	15.7	17.8	2.04	2.19	2.30
41	Nb	Niobium	16.6	18.7	2.17	2.33	2.46
42	Mo	Molybdenum	17.4	19.8	2.29	2.48	2.62
43	Tc	Technetium	18.4	20.8	2.42	2.63	2.79
44	Ru	Ruthenium	19.2	21.9	2.56	2.78	2.96
45	Rh	Rhodium	20.1	23.0	2.70	2.94	3.14
46	Pd	Palladium	21.1	24.1	2.84	3.11	3.33
47	Ag	Silver	22.1	25.2	2.98	3.28	3.52
48	Cd	Cadmium	23.1	26.4	3.13	3.46	3.72
49	In	Indium	24.1	27.6	3.29	3.64	3.92
50	Sn	Tin	25.2	28.8	3.44	3.82	4.13
51	Sb	Antimony	26.2	30.1	3.60	4.01	4.35
52	Te	Tellurium	27.3	31.3	3.77	4.21	4.57
53	I	Iodine	28.5	32.7	3.94	4.41	4.80

Table A. Energies of certain K and L lines in keV (cont'd).

Atomic number	Symbol	Element	Intensity ratio 7 : 1		Intensity ratio 9 : 6 : 1		
			K _α	K _β	L _α	L _β	L _γ
54	Xe	Xenon	29.6	34.0	4.11	4.62	5.04
55	Cs	Cesium	30.8	35.4	4.28	4.83	5.28
56	Ba	Barium	32.0	36.8	4.47	5.04	5.53
57	La	Lanthanum	33.2	38.3	4.65	5.27	5.79
58	Ce	Cerium	34.5	39.7	4.84	5.49	6.05
59	Pr	Praseodymium	35.8	41.3	5.03	5.73	6.32
60	Nd	Neodymium	37.1	42.8	5.23	5.97	6.60
61	Pm	Promethium	38.4	44.5	5.43	6.21	6.89
62	Sm	Samarium	39.8	46.0	5.63	6.46	7.18
63	Eu	Europium	41.2	47.6	5.84	6.71	7.48
64	Gd	Gadolinium	42.6	49.3	6.06	6.97	7.79
65	Tb	Terbium			6.27	7.24	8.10
66	Dy	Dysprosium			6.49	7.51	8.42
67	Ho	Holmium			6.72	7.78	8.75
68	Er	Erbium			6.94	8.06	9.09
69	Tm	Thulium			7.18	8.35	9.42
70	Yb	Ytterbium			7.41	8.64	9.78
71	Lu	Lutetium			7.65	8.93	10.1
72	Hf	Hafnium			7.89	9.24	10.5
73	Ta	Tantalum			8.14	9.54	10.9
74	W	Tungsten			8.39	9.86	11.3
75	Re	Rhenium			8.64	10.2	11.7
76	Os	Osmium			8.90	10.5	12.1
77	Ir	Iridium			9.17	10.9	12.5
78	Pt	Platinum			9.43	11.2	12.9
79	Au	Gold			9.70	11.5	13.4
80	Hg	Mercury			9.98	11.9	13.8
81	Tl	Thallium			10.3	12.3	14.3
82	Pb	Lead			10.5	12.6	14.8
83	Bi	Bismuth			10.8	13.0	15.2
84	Po	Polonium			11.1	13.4	15.7
85	At	Astatine			11.4	13.8	16.3
86	Rn	Radon			11.7	14.2	16.8
87	Fr	Francium			12.0	14.6	17.3
88	Ra	Radium			12.3	15.0	17.8
89	Ac	Actinium			12.6	15.4	18.4
90	Th	Thorium			13.0	15.8	19.0
91	Pa	Protactinium			13.3	16.3	19.6
92	U	Uranium			13.6	16.7	20.2

Table B. Energies of certain M lines in keV.

Atomic number	Symbol	Element	Intensity ratio	
			M_2	M_1
67	Ho	Holmium	1.35	1.38
68	Er	Erbium	1.41	1.44
69	Tm	Thulium	1.46	1.50
70	Yb	Ytterbium	1.52	1.57
71	Lu	Lutetium	1.58	1.63
72	Hf	Hafnium	1.64	1.70
73	Ta	Tantalum	1.71	1.77
74	W	Tungsten	1.78	1.84
75	Re	Rhenium	1.84	1.91
76	Os	Osmium	1.91	1.98
77	Ir	Iridium	1.98	2.05
78	Pt	Platinum	2.05	2.13
79	Au	Gold	2.12	2.20
80	Hg	Mercury	2.19	2.28
81	Tl	Thallium	2.27	2.36
82	Pb	Lead	2.35	2.44
83	Bi	Bismuth	2.42	2.53
84	Po	Polonium	2.50	2.62
85	At	Astatine	2.58	2.71
86	Rn	Radon	2.66	2.80
87	Fr	Francium	2.75	2.88
88	Ra	Radium	2.83	2.97
89	Ac	Actinium	2.91	3.05
90	Th	Thorium	3.00	3.15
91	Pa	Protactinium	3.08	3.24
92	U	Uranium	3.17	3.34

2.4 X-ray line interferences

It can be seen from tables A and B and from sect. 2.3, that certain X-ray lines from different elements (when present in the sample) can be very close in energy and therefore interfere by giving overlapping peaks.

The most usual spectral overlaps are caused by the K_{α} line of element Z-1 (or as with heavier elements, Z-2 or Z-3) having an energy close to that of element Z's K_{α} line. This is the K_{α}/K_{α} interference. Since the $K_{\alpha}:K_{\beta}$ intensity ratio is ca. 7:1 to 5:1, the interfering element must be present in large concentrations, compared to Z concentration, in order to disturb the measurement.

Other interferences are K/L, K/M and L/M. These are less common but the following examples are notorious:



In the arsenic/lead case, lead can be measured from the PbL_{α} line and arsenic from the AsK_{α} line. In this way the unwanted interference can be avoided. However, due to the smaller intensities of these lines, longer measurement times are needed, and these pure element windows have to be set manually (see LIM command).

Other effects to be taken into consideration are secondary emission and absorption, and self absorption. For instance, Cr absorbs strongly Fe and Ni fluorescent radiation, so the Cr atoms see the characteristic radiation from these atoms as exciting radiation. In the end, we receive a bigger signal from Cr in a matrix of iron or nickel than in a matrix of e.g. calcium. Also, self-absorption in some cases can manifest itself. These effects can almost all be compensated for by a thorough selection of samples in the sample calibration and selection of appropriate independent variables into the model.

2.5 Scattered X-rays

The source radiation is scattered by the sample in two different ways: coherent scattering (no energy loss) and Compton scattering (small energy loss). Thus the backscatter peak in figure 2.1 actually consists of two lines close together, the higher energy line being equal to the source energy. Since the whole sample takes part in scattering, the scattered X-rays may yield the most intense lines in the spectrum. It is also obvious that the scattered X-rays must have the highest energies in the spectrum (= source energy).

Note that for special cases, e.g. the Cm-244 source, the backscatter peaks can have a distinguishable energy difference. This should be noted when analyzing elements with characteristic peaks in the high end of the spectrum, because the Compton lines appear in the visible region of the spectrum. The Cm-244 and the Am-241 sources have lines as follows:

	L_{α}	L_{β}	L_{γ}
Cm-244 (Pu L-lines) keV:	(14.3)	18.3	21.4
Compton scattering keV:	(13.5)	17.1	19.7

	K_{α}
Am-241 (Ag K_{α} -lines) keV:	59
Compton scattering keV:	48

Note also, that in the Am-241 source spectrum, a set of low-intensity peaks appear, which are the Np L-lines, and traces from the source capsulation, close to the Fe peak.

2.6 Intensity-concentration relation

The characteristic X-ray line intensity is approximately proportional to the concentration of the element in the sample ($\mu = \mu(C)$).

$$I = \frac{N}{t} = \frac{k \times I_0 \times \tau \times C}{\mu} \quad (1)$$

where:

- I = the line intensity (counts per second),
- N = the net counts (background and overlap subtracted),
- t = the measurement time (seconds),
- k = a constant (includes e.g. the probe-sample geometry),
- I_0 = the source strength (photons per second),
- τ = the excitation cross section for the element in question
- C = the weight fraction of the element
- μ = the average absorption coefficient of the sample

It is obvious from eq.(1) that the stronger the source and the more efficient the probe-sample geometry is, the larger the acquired signal. It is important always to place the sample in the probe in the same way so as to minimize errors due to variation of k . A change in the probe aperture changes k and forces a recalibration (note this when using limiters). Source decay (reduction in I_0) must also be corrected for before it becomes significant. For this, the normalization procedure is used (see command NOR).

The excitation cross section τ (i.e. the efficiency of excitation) varies with the atomic number of the element and with the source energy. A rule of thumb is that the closer the element's analytical line energy is to the source energy, the higher the excitation cross section. The further away the two energies are, the lower the efficiency of excitation. As a consequence, the detection limits are poorer for elements further away from the source energy. See Sect. 2.17 for application ranges of different probes and sources, and appendix for detection limits.

The average absorption coefficient is the weighed sum of the X-ray absorption coefficients of all the elements in the sample. This causes the "matrix effects". Suppose one element has a different X-ray absorption coefficient from the rest of the sample. If that element's concentration varies, it will alter the values of μ , and thus I , of the element actually measured, even though the concentration of the latter may not have changed. This, of course, causes an error in the analysis and such errors are due to "matrix effects". The second element is the "interfering element". The X-MET 880 corrects for such interferences by monitoring also the X-ray intensity of the interfering element, and by applying an empirical correction by choosing this interfering element as an independent variable into the model of the analyte (see Sect. 2.14).

2.7 Counting statistics

The detected X-ray spectrum is affected by random statistics in two ways. The total number of X-ray quanta measured (N) in a time interval has an associated statistical error (one standard deviation = \sqrt{N}), because the number of X-ray quanta emitted from the source and excited in the sample per unit time are statistically distributed. For example, if the total number of counts accumulated in the spectrum, or any preselected part of the spectrum such as a fluorescent peak, is 10000, then its statistical error (one standard deviation) is 100, or 1%. If the total count was 1×10^6 , the standard deviation due to counting statistics would be 1000, or 0.1%.

Errors in measurements due to these "counting statistics" represent the main source of instrumental error in most analyses. Indeed, they set the lower limit of detection for the elements being determined. The reason for this is the escalation of statistical counting errors, because the applicable result is the difference between two counts: peak minus the background. Background is always present (sect. 2.12). Suppose the required net count is $N = P - B$ where P is the gross peak count and B is the background count. The counting statistical error on P is \sqrt{P} and on B is \sqrt{B} , but that on N is $\sqrt{P+B}$ (obtained by squaring the individual errors, then adding and taking the square root). When the net signal N is small compared to the gross peak P (as the background B approaches P) it is clear that the error $\sqrt{P+B}$ can easily approach N in magnitude.

The second effect of random statistics occurs as each detected X-ray photon is converted into a charge pulse in the detector and associated electronic. This causes the sharp X-ray spectral lines to spread into Gaussian-shaped curves as in figure 2.1. The detection process is described more thoroughly in the following section.

2.8 The X-ray detection process

The X-ray detection process involves the following steps: absorption of the X-ray photon in the proportional counter gas filling, formation of an electron avalanche, acceleration of the electrons to the high-voltage wire, conversion to a charge pulse proportional to the X-ray energy E , and a linear amplification of the charge pulse to a range of 0-5 V. Each pulse lasts a few microseconds. In this way each X-ray photon is detected sequentially. The detection rate or total count rate for the X-MET 880 is optimally in the range of 3000 to 6000 photons per second (see command TCR).

NOTE !

For certain applications, counting rates larger than 6000 counts per second must be accepted, e.g. alloy applications. These are easily confronted by changing the maximum count rate under the command EMP/PRM - GENERAL PARAMETERS - Max. Count Rate. The default value is 6 kHz, options at 10 and 15 kHz. Always use count rates below 6000, if possible - either by limiting the sample area with a supplied limiter ring, by filtering the source, or in ultimate cases by changing the source.

2.9 Spectrum accumulation

The first step of X-ray spectrum accumulation in the X-MET 880 memory is to convert the analog pulse height information (voltage) into an 8-bit digital code. This code serves as a pointer to one of the 256 microchannels in the computer memory, and the counts in the microchannel are incremented by one. The spectrum is accumulated over the total count period (measurement time), resulting as a number of counts into that microchannel. This is equivalent to an X-ray intensity (in an energy interval) vs. X-ray quantum energy -histogram.

Figure 2.1 shows schematically X-ray fluorescent and scattered lines with the corresponding detected peaks (dotted) superimposed.

2.10 Spectral resolution

The statistical character of the detection process causes the pulse height to vary randomly around the expected mean value, so that the histogram of pulses from X-rays of the same line energy form a Gaussian curve (figure 2.2).

The spectral resolution is defined as the full width at half maximum (FWHM) of an element peak as per cent of the mean peak energy (figure 2.2). The X-MET superior detectors have a resolution of 13 % measured at the Mn K_{α} line at 5.9 keV.

2.11 The detected spectrum

Figure 2.3 shows schematically an X-ray spectrum corresponding to the X-ray lines of figure 2.1, as recorded by the X-MET 880. The actual spectrum is the sum of the overlapping pulse height distributions of Figure 2.1. Element channels or "windows" are regions (usually of width equal to one FWHM and centered on the peak maximum) selected from a peak either by the program or by the operator during instrument calibration. Notice that the microchannel 255 collects all pulses with an energy above the selected energy range. Thus most counts of the backscatter peak are usually found in this single microchannel. Notice also that to avoid the effects of electronic noise all channels below 35 (approx.) are zeroed out by the electronic. The detector high voltage is normally adjusted so that the practical measurement range is between channels 50 and 200. The energy scale is linear.

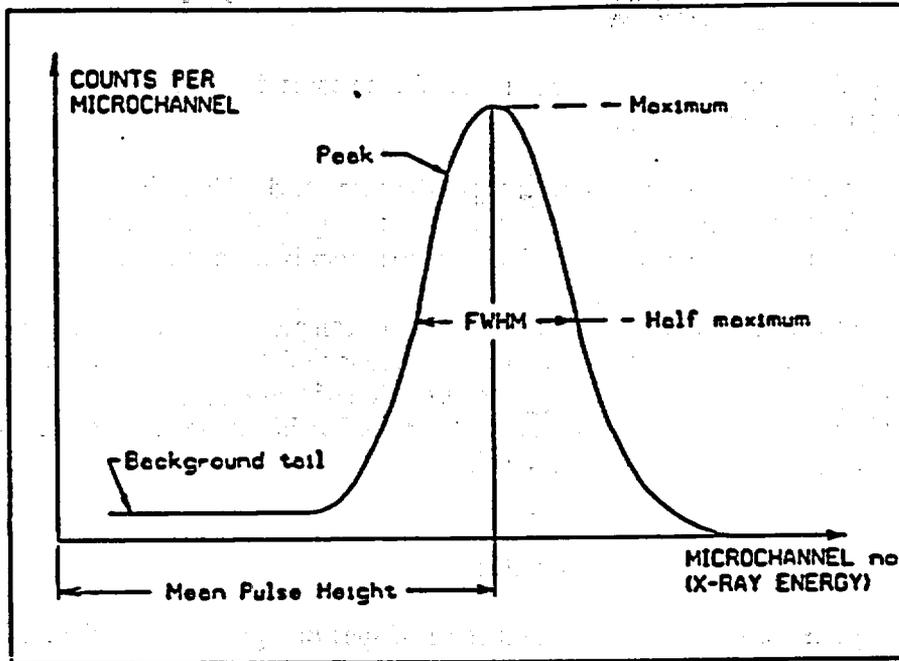


Figure 2.2 Spectral terminology.

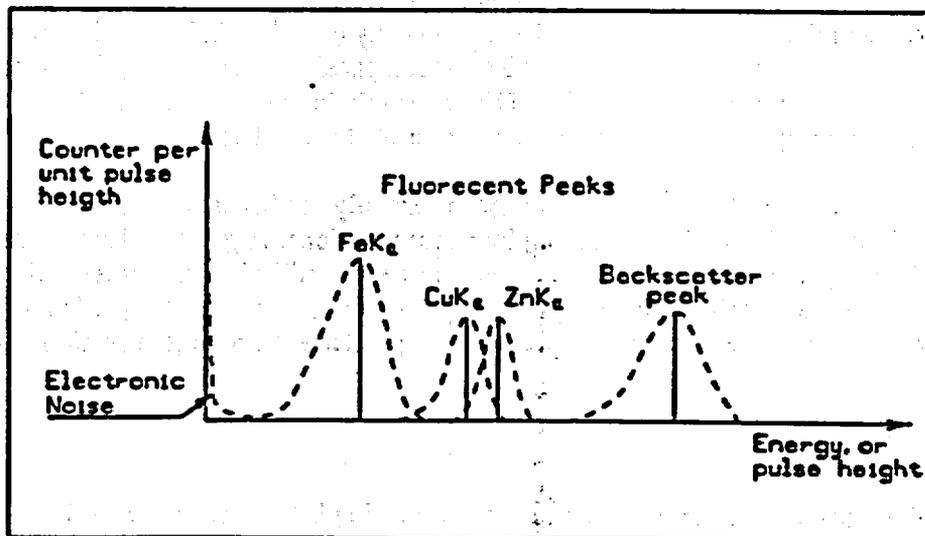


Figure 2.3 The detected spectrum.

2.12 Background and spectral overlap

Most peaks in an accumulated spectrum suffer to some degree from spectral interference due to background and/or overlap.

Background is caused by the low energy tails associated with each peak (see figure 2.2). This results from the imperfect detection process. Its magnitude is proportional to the peak causing it. Most of the background in an X-MET 880 spectrum is from the backscatter peak.

Spectral overlap occurs when two peaks are not completely resolved (as in figure 2.3). The degree of overlap depends on the energy separation of the peaks compared with the spectrometer resolution at that energy. The superior resolution of the Outokumpu Instruments detectors enables K_{α} peaks from elements of adjacent atomic number to be accurately measured even though their energy separation would be small.

2.13 Elimination of background and overlap

After spectral accumulation, the first stage of spectrum processing is the mathematical elimination of background and peak overlap by deconvolution. The data required for the deconvolution calculations is obtained during instrument calibration from the spectra of pure element standards (provided as X-MET 880 accessories), see command PUR. This deconvolution data manifests itself as the G-matrix, see command EMP/PRM.

The deconvoluted pulse counts in each element channel (=window) divided by the measurement time, are called the net intensities (I). (The gross counts in each element channel, before deconvolution, are shown in figure 2.3 as M_1 through M_n).

Note that the subtraction of background and overlap, in whatever manner performed, causes an increase in the statistical error of the net intensity (see sect. 2.7). The larger the degree of overlap and the smaller the measured peak compared to background, the greater is the relative statistical error of the net intensity. The deconvolution process used in the X-MET 880 is mathematically designed to minimize the escalation of statistical errors.

It is of paramount importance to choose carefully the backscatter sample for the model in question, especially when analyzing low concentrations. A good backscatter sample does not contain any elements in the range of the source, but still gives a representative backscatter, similar to the samples to be analyzed. Typically the backscatter sample is Al with a heavy element probe, and a plastic sample with a light element probe (see section 2.17)

2.14 Calculation of concentrations

In the assay mode, the next step in data processing is to convert the net intensities into element concentrations. This is done with a mathematical algorithm using empirical coefficients determined by linear multi-variable regression. The concentration of the element being measured is assumed to be a linear sum of terms. Each term in the equation can be an element intensity or a function of element intensities. The program calculates the coefficients for each term after the intensity terms are chosen (command MOD).

The X-MET 880 contains all the software necessary to calculate the regression coefficients together with statistical criteria to help the operator select the most accurate option in any particular case. Alternatively the calibration can be computed using an external program or, in the simplest cases, with graphical methods, by plotting the measured intensity vs. concentration.

The general equation used in the X-MET analysis to convert net intensities (I_i) to element concentrations (C_i) is

$$C_i = r_{i0} + \sum_{j=1}^6 (r_{ij} \times f_{ij}) \quad (2)$$

A calibration model may include six element concentration equations of this type, each model using up to 10 element channels set in the instrument calibration.

The f_{ij} 's are intensity-related independent variables that can have any of the following forms:

$$f_{ij} = I_m \text{ or } I_{BS} \quad (3)$$

$$f_{ij} = I_m / I_{BS} \text{ or } 1 / I_{BS} \quad (4)$$

$$f_{ij} = I_m * I_k \text{ or } I_m * I_{BS} \quad (5)$$

$$f_{ij} = (I_m * I_k) / I_{BS}^2 \text{ or } I_k / I_{BS}^2 \text{ or } 1 / I_{BS}^2 \quad (6)$$

where m and k are any of the 9 pure element channels, I_m and I_k the net intensities in these, e.g. I_{Fe} is the net intensity in the iron channel, and I_{BS} is the net intensity in the backscatter channel.

Notice that the backscatter channel must be one of the 10 possible pure element channels.

The constants r are the empirical regression coefficients. r_{i0} is called the intercept coefficient, r_{ii} is the slope coefficient for element i, and r_{ij} ($i \neq j$) are the matrix correction coefficients (slopes).

Equation (2) written out results in:

$$C_1 = r_{10} + r_{11}f_{11} + r_{12}f_{12} + r_{13}f_{13} + \dots r_{16}f_{16}$$

$$C_2 = r_{20} + r_{21}f_{21} + r_{22}f_{22} + r_{23}f_{23} + \dots r_{26}f_{26}$$

·
·
·

(7)

$$C_6 = r_{60} + r_{61}f_{61} + r_{62}f_{62} + r_{63}f_{63} + \dots r_{66}f_{66}$$

This algorithm offers many options for accurate concentration calculations when the use of less sophisticated formulae would lead to large errors due to the matrix effects. Two useful and simple variations are described in more detail in the following section.

2.15 Calibration line

When the negligibility of matrix effects is known in advance, or shown by preliminary experiments, all the r_j ($i \neq j$) terms in equation (2) turn out to be zero. The calibration equation then becomes

$$C_i = r_{i0} + r_{ii} I_i \quad (8)$$

where r_{i0} is the intercept coefficient for element i
 r_{ii} is the slope coefficient for element i
 and I_i is the net intensity for element i

To calibrate the instrument, a selection of 8...30 samples of the same chemical and physical form as the unknown samples must be measured to acquire the net intensities I_i , $i=1\dots n$. The inaccuracy of these elements' (reference) concentrations C_i limit the accuracy obtained in subsequent X-MET analyses.

The slope and intercept coefficients for each element are then calculated from the known values of C and I . The calculation can be performed with the X-MET 880, using external calculations, or graphically. The X-MET regression software can do calculations with data from up to 30 calibration samples.

Notice that it is always a good idea to plot the I-C-graph for each element, so that clear typing mistakes etc. can be detected, as well as to facilitate the survey of the physico-chemical nature of the data.

As shown in figure 2.4, the points plotted represent the net intensity vs. the known concentra-

tions for each element. Figure 2.4 is an example for one element. The best straight line is drawn through the plot by minimizing the deviations of the points from the line (a rule of thumb is that an equal number of points should be off the line on each side).

The intercept coefficient is the value of the intersection point this line has with the concentration axis. The slope coefficient is the change of concentration divided by the corresponding change in net intensity along the line.

When significant matrix effects are present, linear matrix corrections will give more accurate results than a simple calibration line. Figure 2.5 shows a typical case of matrix effects discovered as the calibration line was plotted for an element. The variation of iron content clearly has effect on the detected CuK intensities. If the net intensity of iron is included in a linear matrix equation for copper intensity, the errors due to iron interference can be partially eliminated. In this example, because iron clearly effects the slope of Cu, a better equation than a simple line would be as in eq. (9), i.e. the independents would be: 1. Cu ; 2. Fe * Cu

$$\begin{aligned}
 C_{Cu} &= r_{Cu,0} + (r_{Cu,Cu} + r_{Cu,Fe} \times I_{Fe}) \times I_{Cu} \quad \Leftrightarrow \\
 C_{Cu} &= r_{Cu,0} + r_{Cu,Cu} \times I_{Cu} + r_{Cu,Fe} \times I_{Fe} \times I_{Cu}
 \end{aligned}
 \tag{9}$$

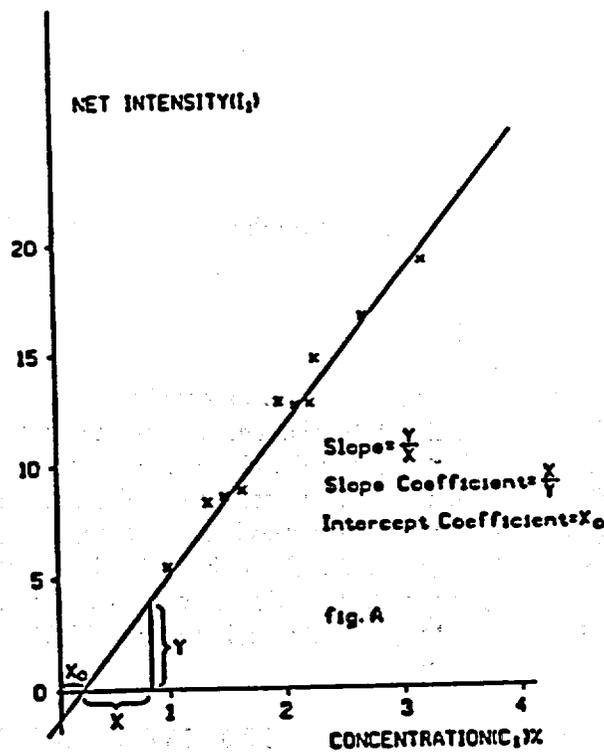


Figure 2.4 Intensity-concentration diagram for a single element (no matrix effects).

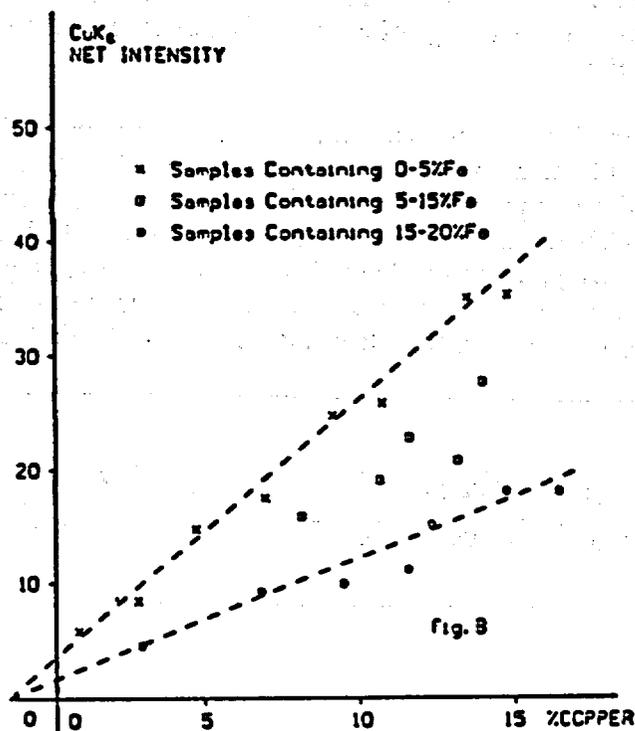


Figure 2.5 Demonstration of matrix effects on the measured intensities.

2.16 Identification from net intensities

The identification of samples is based on a pattern recognition algorithm that uses the information in up to 10 element channels (9 + BS). The intensities of the selected element channels are compared with the information stored in the identification library. Based on this comparison, a test variable, TEST, is calculated for each reference sample. This test variable is in fact a weighted difference of element channel intensities between the unknown sample and a reference sample. The reference with the smallest TEST variable value is chosen as a matching sample. Two threshold values are used in the identification process. The identification rating is determined by comparing TEST with the coarse threshold value (UPPER) and the fine threshold (LOWER).

IF TEST > UPPER the display reads "NO GOOD MATCH FOUND".

IF LOWER ≤ TEST ≤ UPPER the readout is "POSSIBLE MATCH".

IF TEST < LOWER the readout is "GOOD MATCH".

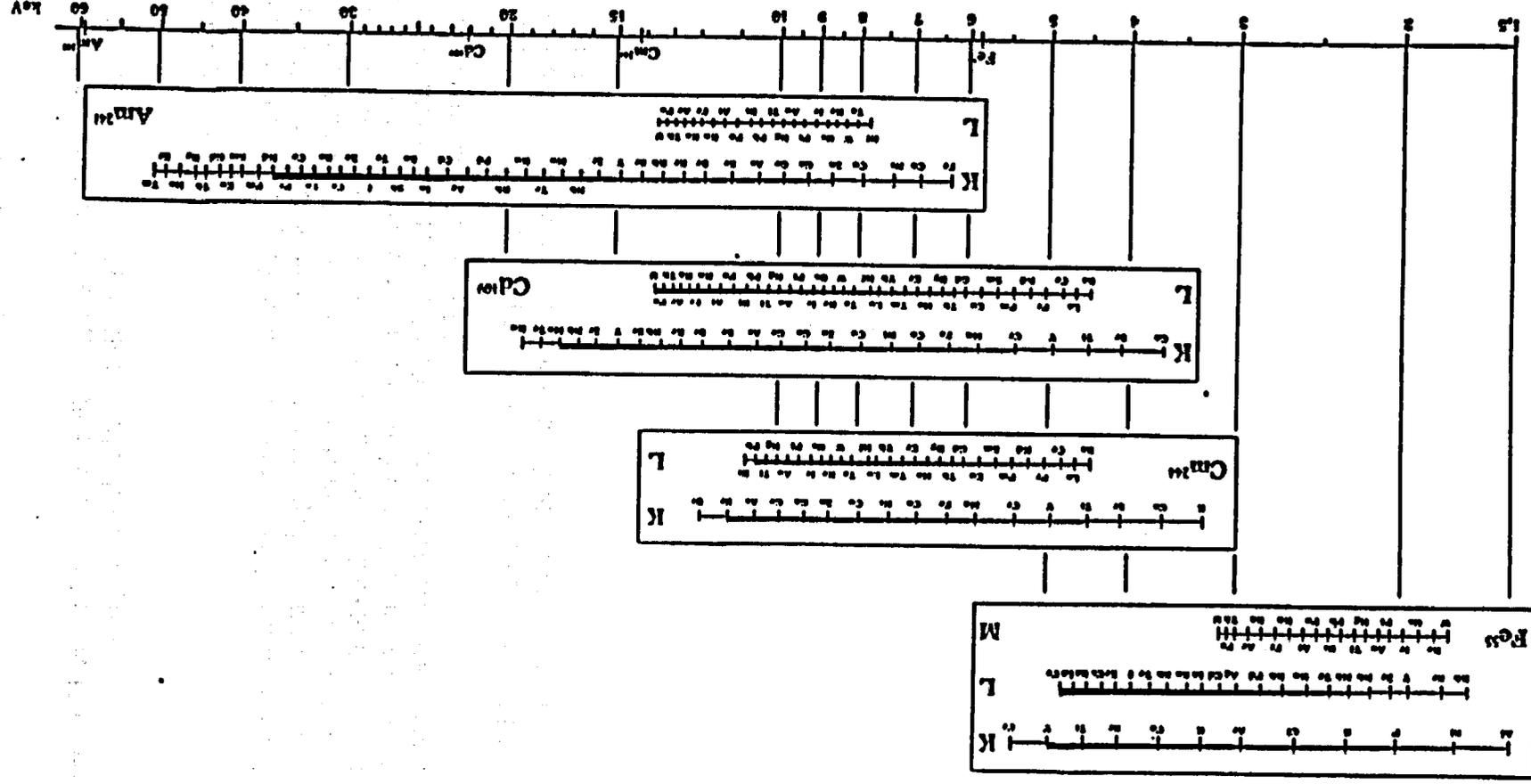
The threshold values can be selected by the operator, see command THR, the default values are in THD.

In the case of a POSSIBLE MATCH, often a first and a second choice identification reference is given and displayed. The value of the TEST variable is also displayed.

2.17 Application ranges of probes

Flexible and versatile analysis performance is obtained from the use of five probe types: HEPS, SAPS, LEPS, SLPS and DOPS. Four different source types are available for these: Fe-55, Cm-244, Cd-109 and Am-241. The Fe-55 source is used in the light-element probes LEPS and SLPS or as the second source in dual-source heavy element probe DOPS; the other heavy element probes can use Cm, Cd or Am sources as desired. Hence elements from aluminum to uranium can be analyzed using two to three probes. The probe and source combination for each purpose can be selected on the basis of figure 2.6.

The elements shown on the emphasized axis in figure 2.6 are those for which the source is particularly suitable. The elements on the unemphasized axis can be analyzed but the results are not of the same accuracy.



2.18 Bibliography

- /1/ Principles of Quantitative X-ray Fluorescence Analysis, R Tertian and F Claisse, Heyden and Son Ltd, 1982, 385 pp.**
- /2/ X-ray Fluorescence Analysis of Environmental Samples, T G Dzubay, Ed, Ann Arbor Science, 1977, 310 pp.**
- /3/ Radiation Detection and Measurement, G F Knoll, John Wiley and Sons, 1979, 816 pp.**
- /4/ Applications of a New Multielement Portable X-ray Spectrometer to Materials Analysis, C von Alfthan, P Rautala and J R Rhodes, in "Advances in X-ray Analysis", Eds J R Rhodes et al., Vol 23, pp 27-36, Plenum Press, 1980.**
- /5/ Application of a Microprocessor-based Portable XRF Analyzer in Minerals Analysis, J R Rhodes and P Rautala, International Journal of Applied Radiation and Isotopes, Vol 34 No. 1 pp 333-343, Pergamon Press 1983.**

3. THE PRINCIPAL COMPONENTS OF THE ANALYZER

3.1 Introduction

The X-MET 880 is a mains/battery operated field and laboratory analyzer. It is based on energy dispersive X-ray fluorescence technology, and on the use of radioactive isotopes. The X-MET 880 provides a method for contents analysis or sample type identification (sorting) directly from solid, powder, liquid or briquette samples. The X-MET 880 can hold up to 32 calibrated models, 400 identification reference spectra and 20 pure element spectra in its memory at the same time.

The measurement principle is based on energy dispersive X-ray fluorescence (EDXRF). The radiation from a radioactive source strikes the sample and excites fluorescent radiation (figure 3.1). The spectrum of the fluorescent radiation, i.e. the radiation intensity-vs.-energy graph, contains the information required for qualitative and quantitative analysis of the sample. The radiation is measured with a proportional counter and the data is processed by a microcomputer in the electronic unit. The result is displayed as an analysis (composition along with element symbols) or as the sample type designation (identification) in alphanumeric form.

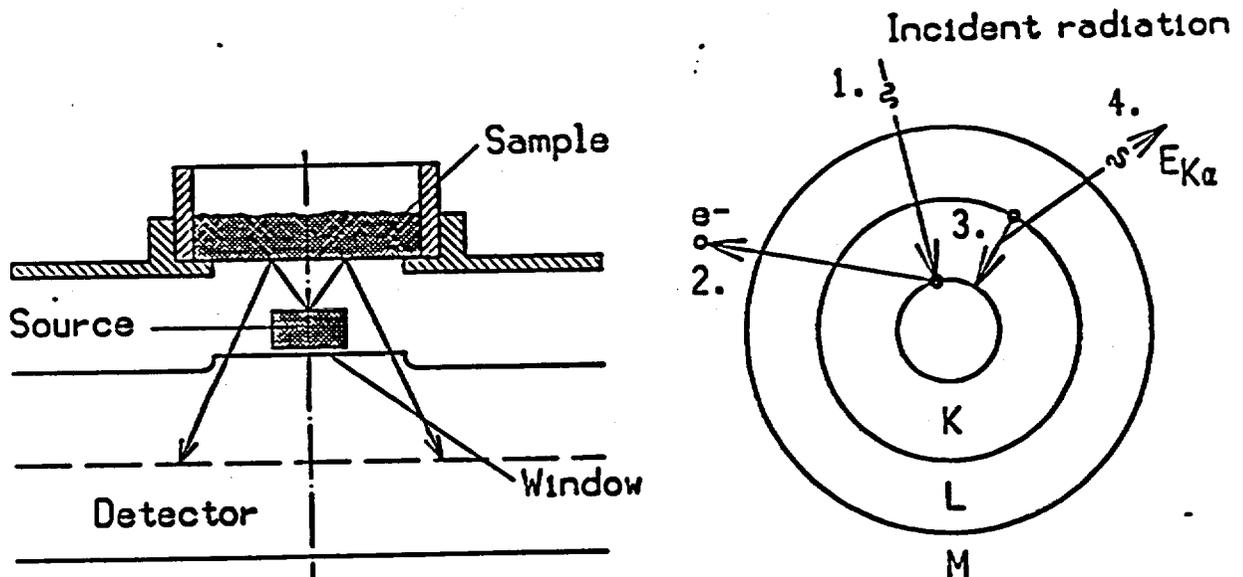


Figure 3.1 The principle of the X-ray fluorescence excitation process

3.2 Analyzer set-up

The analyzer consists of one or several probes, an electronic unit and accessories such as sample cups and plastic film. Different probes are available for various applications. The analyzer can be used to measure elements within atomic numbers 13 to 92, i.e. from aluminum to uranium.

The analyzer can flexibly be calibrated to measure the elements in most any application. A concentration model can be set up to provide a simultaneous concentration analysis for 1 to 6 elements. See appendix for detailed detection limits of different sources and elements. Note, that the matrix always affects the detection limits, as also interfering elements do.

Data from up to 400 reference samples can be stored in reference libraries, and then be used for the identification of unknown samples. The identification is based on information measured from up to 10 element channels. The identification results are shown as the closest measured reference sample in the library.

3.3 Power supply options

NOTE! USE ONLY BATTERIES AND CHARGERS SUPPLIED BY OUTOKUMPU INSTRUMENTS!

The capacity of the X-MET lead battery XBPS 2163 is sufficient for max. 10 hours (20°C) of use when fully charged. The monitoring of the battery charge level is automatic: when the voltage falls below the first threshold level, the warning "BATTERY LOW" is displayed. Should the battery not be replaced, it runs out in ca.30 minutes and the instrument switches off. The first warning can be acknowledged with the CONT/YES key to continue operation. **NOTE !** After a "BATTERY LOW" message has been displayed, the battery should be charged as soon as possible, to prevent the battery from going into a "deep discharge" state. If it cannot be recharged within the same day, remove the battery from the electronic unit until charging is possible.

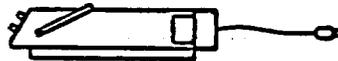
Mains operation is possible by using the X-MET charger unit XBCS 2164 (standard accessory). The mains voltage values are 230V \pm 20% or 115V \pm 20%, depending on the position of the selector switch on the side of the charger. See figure 3.5 for details of changing the mains voltage. For mains operation, simply connect the charger to the battery cassette in the analyzer. The charger can also be used to charge a spare battery while the analyzer is operated with another battery. The mains operation is recommended whenever possible. **USE ONLY XBPS 2163 BATTERIES. DO NOT ATTEMPT TO CHARGE OTHER BATTERIES WITH THE XBCS 2164 CHARGER.**

The battery charging voltage is also adjusted automatically to ensure maximum battery life. A LED on the end of the charger shows current setting, e.g. TRICKLE CHARGE means the battery is fully charged. If the instrument is ON, the LED will show NORMAL current even if the battery is fully charged.

The analyzer can also be used on a 12V to 24V car battery with a separate battery cable (accessory) plugged directly to the power supply connector of the XAES electronic unit (behind the battery pack). **DO NOT ATTEMPT TO CONNECT THE BATTERY CABLE TO THE X-MET BATTERY CASSETTE.**

NOTE ! Do not unplug the battery pack with the instrument switched ON.
Keep a battery connected to the electronic unit whenever possible !

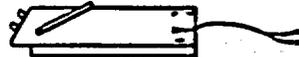
AC outlet operation



Battery operation



Spare battery +
charger



External battery
straight to X-Met

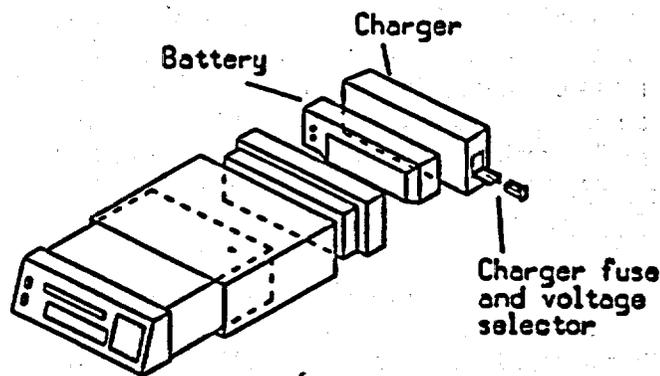
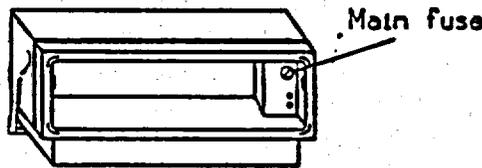


Figure 3.2 X-MET power supply options.

3.4 XAES electronic unit

The information from the probe is processed in the electronic unit which uses a multiprocessor system. A 5 V lithium back-up battery is located inside the electronic unit to supply the program circuits power in case the main external battery is removed. The functions are controlled by means of a membrane keyboard on the front panel and the results are displayed on a 40 character two-line LC display. All calculations are processed with the accuracy of 7 digits although results are shown rounded. The front panel has connectors for the probe cable and an external data communications serial port (figure 3.3). Space is provided at the bottom of the unit for storing accessories and a surface probe.

3.5 Front panel description

NO	DESCRIPTION
----	-------------

KEYBOARD

- | | |
|----|----------------------------------|
| 1 | Power 'OFF' switch |
| 2 | Power 'ON' switch |
| 7 | Numeric keys (O-Z with shift on) |
| 10 | START |
| 11 | RECALC |
| 12 | MODEL |
| 13 | M.TIME |
| 14 | Backspace |
| 15 | Shift toggle on/off |
| 16 | Previous line |
| 17 | END/NO |
| 18 | CONTINUE/YES |
| 19 | Space |

DISPLAY

- | | |
|---|---------------------------|
| 3 | Alphanumeric LCD display |
| | Display read-outs: |
| 4 | Selected measurement time |
| 5 | Selected model |
| 6 | Shift on |

CONNECTORS

- | | |
|---|-------------------------|
| 8 | RS-232 serial interface |
| | Probe connector |

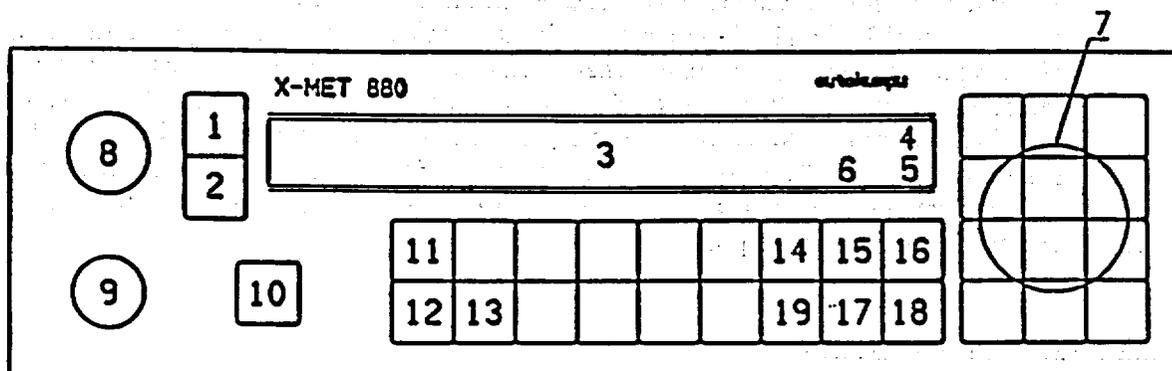


Figure 3.3 X-MET 880 front panel.

3.6 Keyboard

The analyzer has a 33-key membrane keyboard (figure 3.3). The keyboard ON and OFF keys, editing keys END/NO, CONT/YES, SHIFT, ◀ and ▶, and 11 other special function keys:

CTRS+ CTRS-	= LCD contrast adjustment
F1 F2 F3 F4 F5	= user definable function keys
START	= start measurement
MODEL	= select working model
M.TIME	= select measurement time
RECALC	= repeat calculation of collected intensities with a selected model

Other commands are entered as strings of three characters.

Alphanumeric commands and responses are executed after pressing the CONT/YES key. In general, the CONT/YES key means a positive reply, or a command to proceed. END/NO, respectively, means a negative reply or termination of a function. Occasionally several CONT/YES or END/NO key pressings are needed to get back to the prompt >.

The SHIFT key toggles the keyboard between the character and command/digit modes. SH is

displayed in the lower right hand corner of the display when shift is ON and the characters mode is in use. ← erases the character left to the cursor, ▲ is used to scroll the multi-line display backwards (in certain commands only, e.g. ASY).

The keyboard can be locked by entering the command LOC. In this state, the keys will function normally, but the X-MET will not accept the commands given, except EMP/UNL to unlock the keyboard. Also, the function keys F1...F5, and the "standard" commands operating on a single keystroke, e.g. M.TIME work.

3.7 Display

The display is an alphanumeric LC display with two lines of 40 characters each. The display shows continuously the number of the current model in the lower right-hand corner, the shift on with a SH, and the measurement time in the upper right-hand corner.

After completing a measurement in a calibrated model, the results are displayed in an alphanumeric form; concentrations with the element symbols, or a matching ID reference. Note that the units of concentration are not displayed, as they are by definition the same as those of the calibration samples. During a measurement, the remaining measurement time is indicated on the display. Any warnings or error messages from the internal test routines of the instrument are displayed in an alphanumeric form.

Since the operating software is interactive, the display is used to give prompts to the operator. All displayed information (and more) can be output to a printer or terminal through the serial port.

The display contrast can be adjusted, using the keys marked CTRS- and CTRS+, as necessary. The display can also be backlit to enhance the readout. This feature can be toggled on and off using the command BLT. **NOTE !** The display gives the results of each element with four digits only: if more digits would be needed, a display of **** will appear (i.e. 9230 ppm will be displayed, but 10 000 ppm will cause a display of ****).

3.8 Front panel connectors

3.8.1. Probe connector (PROBE)

This is where the probe is to be connected. All probe types can be used with the same electronic unit. Each probe is individually identified by coded information passed through the connector. This allows the recognition of up to six different probes.

A more flexible use of up to three probes is possible with the mechanical distribution box (XDBS), and up to six probes can be used with the electronic distribution box (XEDS).

NOTE ! All probe connections must be made while the analyzer is in the OFF state.

3.8.2. IN/OUT connector

The electronic unit contains a RS-232C serial interface and a 0-5 V analog output. The serial interface is used for sending or receiving information to/from a printer, a data terminal or an external computer. The interface can be used for external control of the instrument, printout of the measurement results etc. The analog output is under software control and can be used to drive e.g. x-y-plotters, see command CAO, configuration of analog output.

The serial interface can be used together with the instrument's own keyboard and display. All the text displayed in the LC display will also be transmitted to the serial port.

The communication parameters for the IN/OUT connector are set as follows. An external terminal or printer must be set to the same specifications.

8 data bits
1 stop bit
No parity
Baud rate 300 (see below)

The baud rate of the serial interface can be set using the command CSI (Configuration of Serial Interface). The baud rate can have values 50, 75, 110, 134.5, 150, 200, 300, 600, 1200, 1800, 2400, 4800, 9600 and 19200 bauds. After stepping forward (CONT/YES) or backward (▲) a new baud rate and the enquiry NEW? appears on the display. The END/NO key finishes the enquiry and selects the last displayed baud rate.

Serial port connection cables are available. The cable has a round connector for the X-MET port and a 25-pin D-connector of the selected type at the other end.

Communication cable code	Type of connector on the cable
3877 453	Male (std. accessory)
3877 420	Female

More information on communication can be obtained from the maintenance manual or from Outokumpu Instruments.

3.9 Probe types

3.9.1 HEPS Heavy element probe set

The probe is used for the analysis of elements from Ca to U in powder, briquette, film, solid or liquid samples. The probe contains a Cm-244, Cd-109 or an Am-241 radiation source, a detector, and the probe electronics. The sample holder is covered by a lid. When the sample holder, or measurement carriage, is in the front position, the isotope source is covered, and the sample can be changed safely. When the lid is closed, and the carriage pushed to the measurement

position, the source is revealed and a measurement can be made. The front position is also the gain control position. The film on the sample cup holder is of the same film as in the sample cups, and should be kept clean and intact.

3.9.2 LEPS Light element probe set

The LEPS probe is similar to the HEPS probe in appearance. It is equipped, however, with a light element detector and a Fe-55 radiation source of special design. It is used for the analysis of K-lines of light elements from Al to V, or, in special cases, up to Cr, as well as for elements from Nb to Sb (L-lines). The film in the sample cup holder is the same film as in the sample cups.

3.9.3 SAPS Surface analysis probe set

The surface probe is used for the analysis of elements from Ti to U direct from the surface of a sample. Like HEPS, the SAPS can contain a Cm-244, Cd-109 or an Am-241 radiation source, a detector, and the probe electronics. A special pure element sample holder is supplied as a standard accessory.

The SAPS surface probe is the predominant probe in field use. For transport it is stored in a drawer under the electronic unit. It is equipped with a 2.3 m cable, with a 5 m option. For slim objects like pipes and rods it can be equipped with a slit window (6 x 21 mm or smaller).

The slim design of the probe allows measurements on narrow objects such as rods and wires, and in confined areas such as welds inside corners with the least possible geometric error. The probe is easy to hold against a sample surface. The measuring window is covered with a plastic foil, with a shutter behind it. When the trigger is pulled, the shutter opens. Pulling the trigger to the end starts a measurement. The shutter position is shown by the mechanical indicator on the side of the probe. The colors are as follows: green - shutter closed; red - shutter open.

The indicator light in the handle is red during the measurement. If the shutter does not stay sufficiently open, the light goes out and the measurement is interrupted.

The probe is provided with a safety lock which can be mounted to the handle. In locked position the shutter can not be opened.

DANGER !

While the shutter is open, the probe presents a radiation hazard if the source window is not held against a protecting surface.

The revealed source must not be pointed at a person or anything that might be damaged or effected by radiation.

3.9.4 DOPS Double source surface probe set

The double source surface probe is used for analysis of elements from Ti to U. DOPS uses a combination of two sources, usually Cd-Fe or Am-Cm, for an extended element measurement range. The probe alternates the sources automatically, or measures with one source only, as required. The ranges of the two sources are not fully covered with a Cd-Fe combination, the measurement range starting at Sn (L-lines), to Mo, and not starting from Al.

The DOPS probe provides the same versatility and ease of use as the SAPS surface probe. The two probes have a similar appearance, and the DOPS fits in the storage holder underneath the electronic unit, too. It can also be fitted with either a 2.3 m or a 5 m cable, and a slit window for narrow objects (9 x 21 mm).

As the dynamic range of the probe is much wider, there are certain details to follow in the calibration. See chapter 5 for DOPS calibration details. The operating instructions and cautions concerning the use of the SAPS apply equally to the DOPS.

3.9.5 SLPS Surface light element probe set

The probe is used for the analysis of light elements from Al to V, or in some cases to Cr, as well as for elements from Nb to Sb, directly from the surface of a sample. The probe contains a special light element detector, a Fe-55 radiation source, and the probe electronic.

The radiation source is located in the bottom of the probe behind a protective shutter. The shutter opens as the probe is pressed against the sample surface. The green light on the probe handle turns red when the shutter is sufficiently open. If the light turns green before the end of the measurement, the shutter is not properly open and the measurement is interrupted, and must be started again. Watch out for the protective film at the bottom, as it is not changable from the outside.

DANGER !

While the shutter is open, the probe presents a radiation hazard if the source window is not pressed against a protecting surface. The revealed source must not be pointed at a person or anything that might be damaged or effected by radiation.

3.10 Distribution boxes

Two types of distribution boxes are available: XEDS 2307 electrical distribution box, and XDBS 2167 mechanical distribution box.

The XEDS 2307 electrical distribution box supports up to six different probes of any type at a time. Probe selection is done mainly through the model automatically, with a special command (SPR), or interactively before a command is executed. The IN/OUT-connector of the X-MET 880 is used for controlling the distribution box; simultaneous use of a terminal, printer etc. is possible though, through the distributor box itself.

The XDBS 2167 mechanical distribution box supports up to three different probes of any type at

a time. Probe selection is done manually using a switch on top of the distribution box.

The advantage of using a distributor box is in avoiding the shut-down of the instrument, and subsequent warm-up, when changing probes. The electrical distribution box performs automatic gain control for all the connected probes, and thus renders each probe ready for use immediately. With the mechanical distribution box, a manual switch is used to point the probe in action. Gain control for that probe is performed after a) a measurement; b) a probe is selected with SPR command; c) the EMP/PRP command is given; d) the PUR command is given; e) EMP/PCT is given. This is in order to tell the instrument that the probe has been changed.

3.11 Illustrations

The following illustrations are provided here:

Figure 3.4 HEPS probe exploded view.

Figure 3.5 LEPS probe exploded view.

Figure 3.6 SAPS probe exploded view.

Figure 3.7 DOPS probe exploded view.

Figure 3.8 X-MET with electronic distributor box and various probes.

HEPS probe

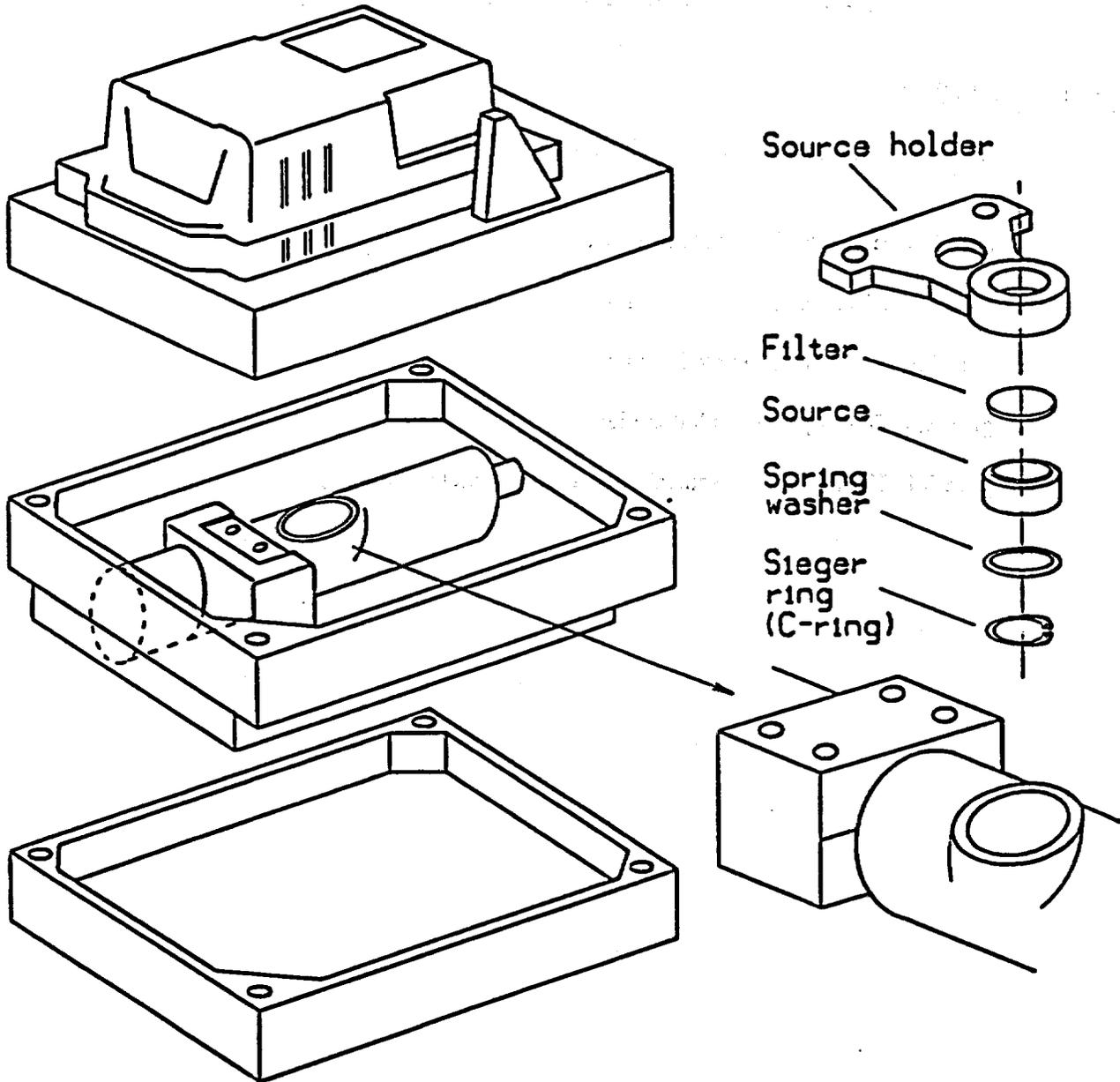


Figure 3.4 HEPS probe exploded view.

LEPS probe

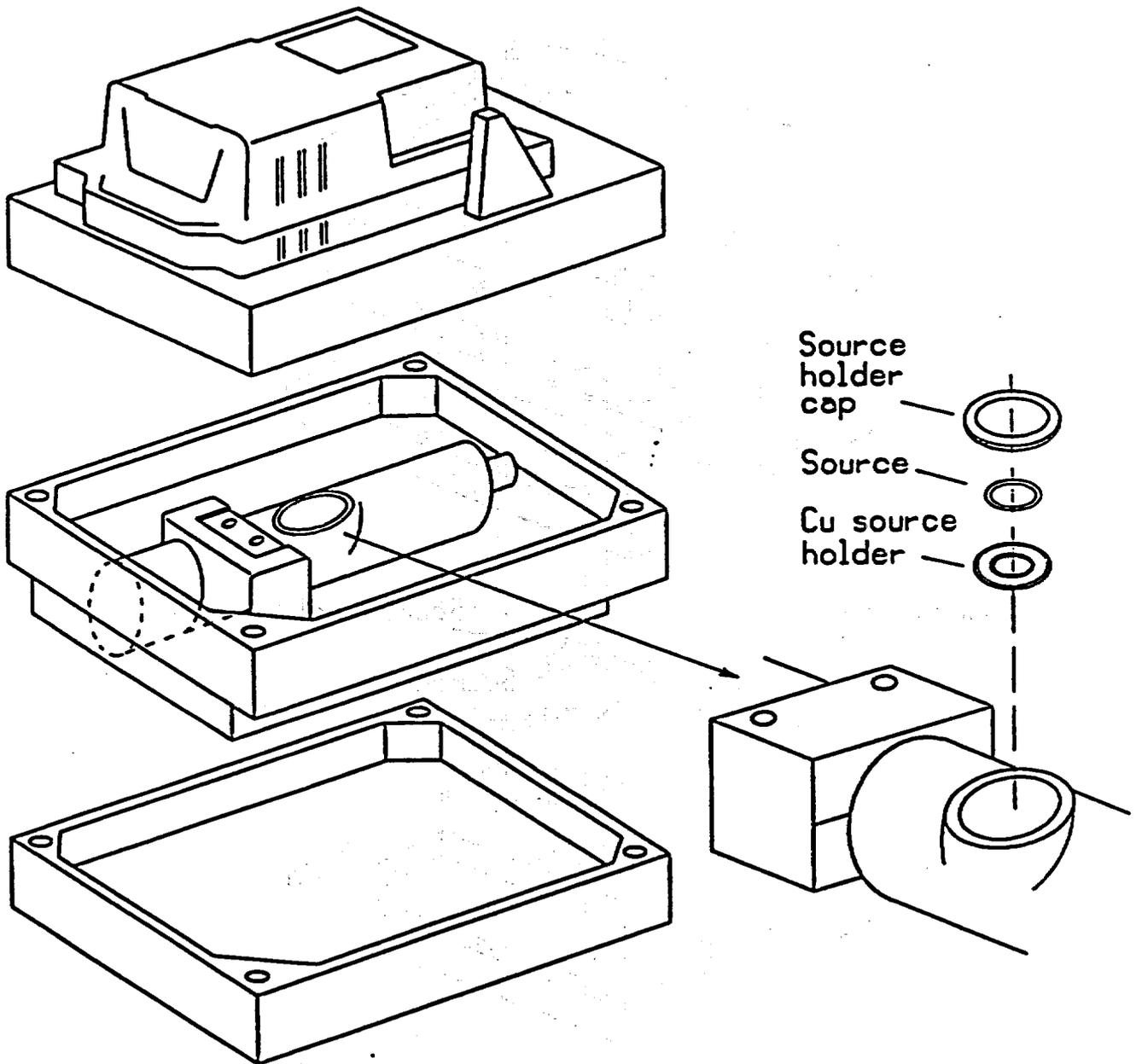


Figure 3.5 LEPS probe exploded view.

SAPS probe

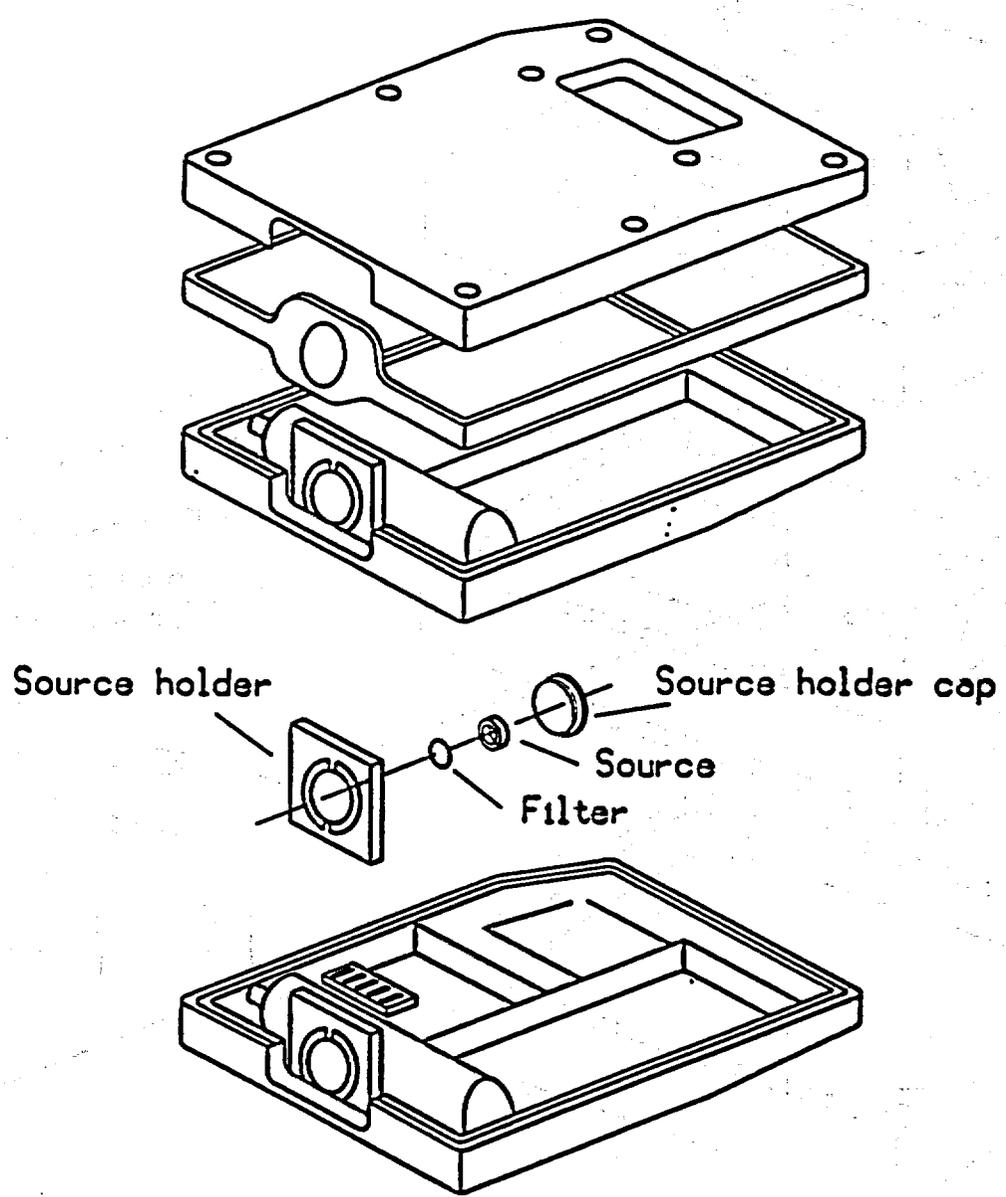


Figure 3.6 SAPS probe exploded view.

DOPS probe

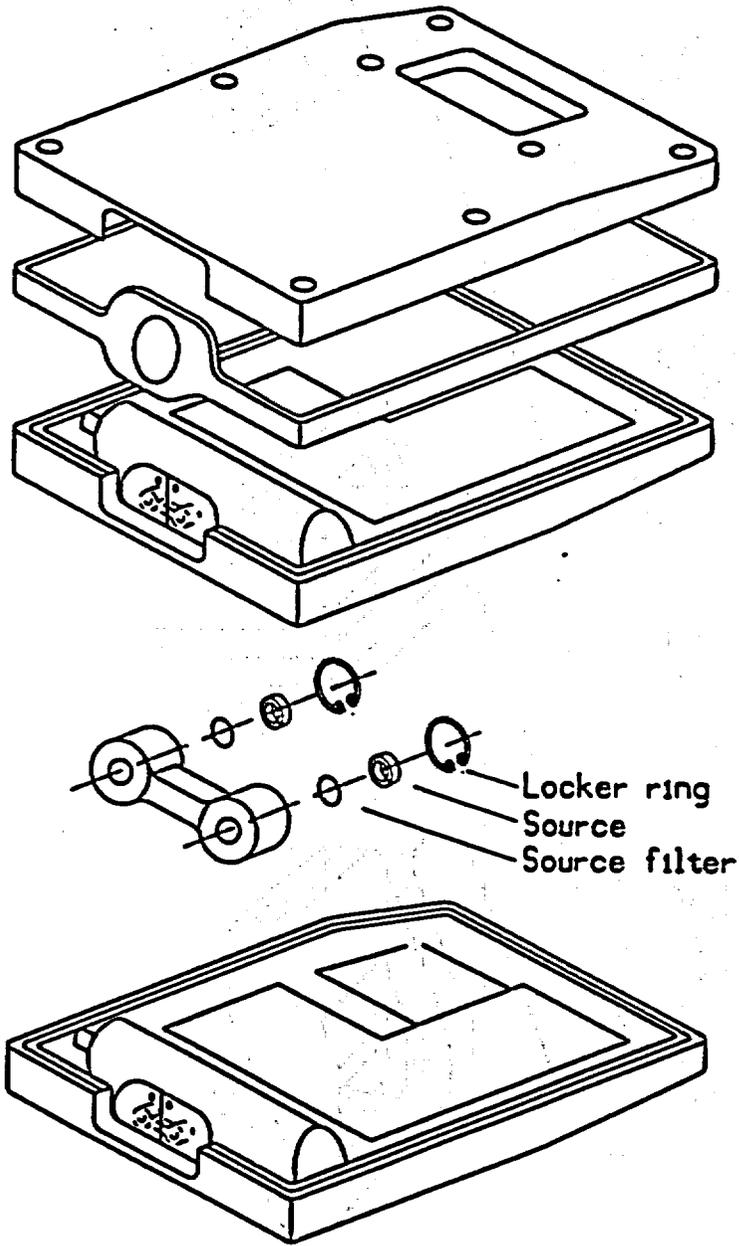


Figure 3.7 DOPS probe exploded view.

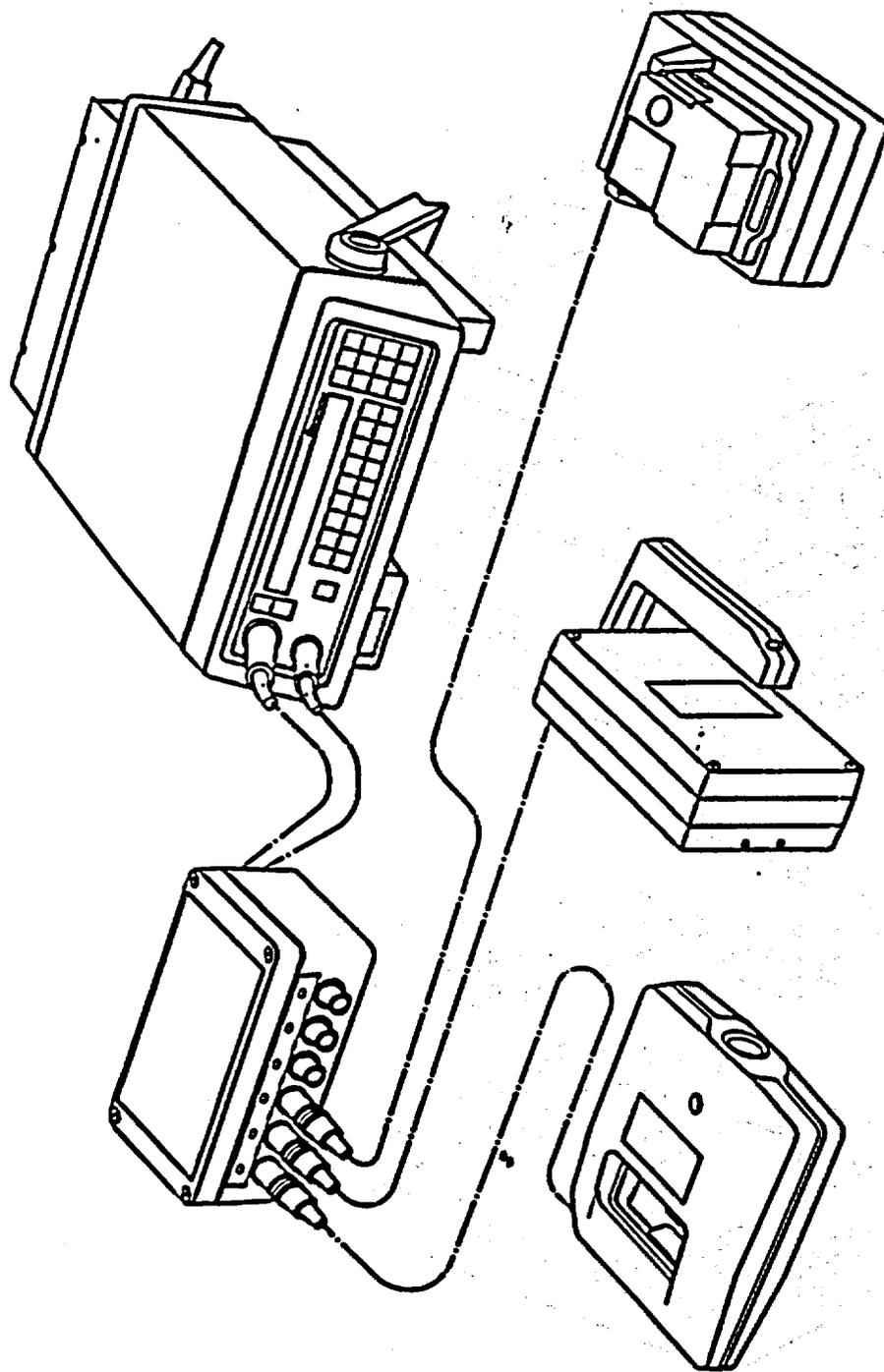


Figure 3.8 X-MET with electronic distributor box and various probes.

4. PRE-OPERATING INSTRUCTIONS

4.1 How to get started

1) Check that the battery pack of the analyzer is in its place. Ensure, that the charger voltage selector is at the correct setting. If not, change the voltage setting to the correct value, see fig. 3.5. Connect the charger to the electronic unit by fitting its plug into the opening in the battery (under a rubber plug), and the power cord to a power outlet. Consequently, a LED on the charger should be lighted. If not, check the power cable connections at both ends, the charger fuse, and the power outlet. Try another cable if possible.
The analyzer can also be supplied from a car battery at 12 to 24 volts, straight to the X-MET. Refer to sect. 3.3.

2) Connect the probe to the PROBE connector. If several probes are to be used, they can be connected through a distribution box. Do not apply power before the probe(s) has been connected.

3) Apply power to the instrument by pressing the ON button. This initiates the internal self-test routine of the instrument:

```
X-MET 880 V. 1.0.1 6.1.1989  
> SELF TEST COMPLETED
```

Do not worry about the error message GAIN C.: COUNT RATE TOO LOW, PRI, which will appear if the probe has been initialized (command INI). It will disappear after about 5...20 sec. (Should it not disappear, contact a representative of Metorex Inc.)

The > prompt at the beginning of the line indicates that the analyzer is ready to accept operating commands.

Check, that no error messages remain on the display.

4) Choose the appropriate model number you want to work with, using the MODEL key.

5) After power-on, the instrument requires a stabilization time of about 30 min. in the ON state, with the probe(s) in the gain control position (this is to acquire maximum accuracy). The stabilization time required after a considerable change of temperature is about 30 min/20°C temperature change.

6) After stabilizing, the instrument is ready for use.

4.2 Probe operation

4.2.1 HEPS and LEPS probes

Pull the measurement carriage to the front position, so that the lid can be opened. The probe is now in the gain control position. (sect. 5.1.3) The X-MET now performs a complete gain control sequence in 5 minutes.

It is advisable always to leave the probes in gain control position, when not measuring. If the

probe initialization has not been carried out, perform initialization according to section 4.2.3.

4.2.2 SAPS, DOPS and SLPS probes

Release the trigger on SAPS and DOPS probes. Place the probe so that the shutter remains closed, that is, on its side. The probe is now in the gain control position, (sect. 5.1.3) The indicator light (SLPS) or the mechanical indicator (SAPS, DOPS) shows green. The X-MET now performs a complete gain control sequence in 5 minutes.

4.3 Probe initialization (INI) OR ING WHEN USED WITH C-8 - ONLINE PROBES

The initialization of the probe is a very important feature, so read this carefully.

To make the instrument recognize a probe, and to render it active, each probe has to be initialized.

CAUTION: Do not initialize a probe that has already been initialized and used to calibrate models. Re-initialization in such cases may require all calibrated models to be recalibrated. On X-METs calibrated at the factory, the probe is already initialized, and should be recalibrated only in following cases:

- 1) You have added a new probe to the X-MET
- 2) You have a new source, or your source has been filtered (do not confuse sample limiters with source filters)
- 3) You have a new detector in your probe
- 4) You have got the error message "GAIN CONTROL: GAIN OUT OF RANGE", and the gain value is 0 or 255
- 5) You have to recalibrate the instrument for some reason

The initialization procedure is simple: let the instrument and probe to warm up for 30 minutes, in the gain control position, and give command INI. The instrument will measure the internal reference for 60 s, and report the peak channel limits. Also, the user has to select a number (1...6) for the probe, and assure that the number used is "free", i.e. not used for another probe. A list of probes initialized can be displayed on a terminal by giving command EMP/PRP, CONT/YES, and after the prompt PROBE X? give P and CONT/YES.

Initialization sets the initial values for the probe gain control parameters. The initialization must be performed separately for each probe. So, initialization is only performed once for each probe: when starting the calibration of the first model. If the initialization is renewed, it may be necessary to do the calibrations of all models associated with the probe again.

1) To carry out initialization, first place the probe in the gain control position. The source is covered by the shutter. Let the instrument stabilize.

2) Start the initialization by entering INI. First prompt is for the normalization method used. Pressing CONT/YES confirms the choice. Choosing manual normalization means, that the effects of the source decay are compensated for manually (see command NOR). Autonormalization is currently not recommended. Use the manual normalization option.

Example of the initialization procedure:

```
> INI
PROBE NUMBER 1? 3 (You want to initialize as probe no.3)
NORMALIZATION: AUTO? END/NO (do not use autonormalization)
NORMALIZATION: MANUAL? CONT/YES
INITIALIZE? CONT/YES
MEASURING: PROBE 3 TYPE HEPS
60 SECONDS LEFT (countdown)

GAIN CHANNEL: 94 TO 115
>
```

When initializing a DOPS probe, you are also prompted to give the ratio of the measurement times of the two sources. The source with the higher energy is designated as the A source, and the one with the lower energy as the B source. A ratio of $B/A = 2$ means that the measurement time of the B source is twice that of the A source. A time ratio value differing from one is usually needed in special applications only.

After the initialization measurement, a channel range is displayed. This is the range under inspection in the gain control. At least 5 minutes must now be allowed for the gain control to operate before the pure element calibration.

4.4. Pure element samples

A pure element sample contains only the element of concern. These are supplied by Metorex Inc. , according to customer application.

A backscatter (BS) reference sample allows assessment of the amount of reflected (scattered) radiation, which creates most of the background (noise) on the measurement of each element. A backscatter reference sample effectively reflects radiation as the true samples do, but does not contain any elements in the range of the source.

A suitable scattering reference sample for the heavy-element probe is e.g. an Al or Si pure element sample, a very low concentration tailings sample, a pure gasoline sample for Pb in gasoline measurements, a pure base-oil in oil additive measurements etc. A light-element probe backscatter sample can be distilled water, pure decanol, paraffin oil, or a plastic slab, depending on the application. For liquid samples it is advisable to use a liquid BS sample, and for solids a solid sample, for powders a powder sample, if applicable.

A pure element reference sample must be handled with care in order to prevent contamination. Keep them in the boxes supplied.

Natural pure element samples (from Al to U) are available from Metorex Inc.

4.5 Collecting and preparing calibration samples

4.5.1 Calibration samples

Calibration samples are necessary in performing the calibration of the X-MET analyzer. Chapter 5 describes the calibration process in detail.

Calibration samples must be representative for the application in case. This implies mainly two considerations: 1) all the elements (elements to be analyzed + main interfering elements) must be present in the calibration samples in the concentration ranges of the samples to be analyzed, and 2) the particle size distribution must be similar (particle size). Moisture content has importance only when analyzing elements below Fe (assuming non-slurry samples), or low concentrations, such as ppm levels.

The actual concentrations of assay model calibration samples must be known through a sufficiently accurate method, e.g. wet chemical analysis, wavelength dispersive XRF etc. Concentrations of the identification model samples need not be known.

4.5.2 The number of calibration samples required

For an assay model, the amount of samples required depends on

- * the number of analyzed elements m (1-6).
- * the number of required dependent variables n for the model equation of each analyzed element (1-6).

Generally, for a reliable model, the number of samples has to be much greater than the number of independents in the model for that element. Should it not be greater than that, X-MET prompts during calibration modelling an error message **TOO MANY INDEPS FOR THESE POINTS, CHECK INDEPENDENTS** or gives $R = 1.000$ $S = ****$ $F = ****$.

The model also corrects for matrix effects. This requires for combinations of samples with different quantities of different elements. If no matrix correction is needed and the simple calibration line model is usable, 5 to 10 samples are enough (e.g. a heavy element alone in a light matrix like water or hydrocarbon). If more than two elements are to be analyzed, the number of samples should be at least 15, or better, 20-30. See table C.

Table C Recommended number of calibration samples.

Independents → Elements (analytes)	1	2	3	4	5	6
1	7...10	7...10	10...15	15...20	> 30	> 30
2	7...10	7...10	10...15	15...30	> 30	> 30
3	7...10	10...15	10...15	15...30	> 30	> 30
4	7...10	15...30	15...30	15...30	> 30	> 30
5	7...10	> 30	> 30	> 30	> 30	> 30
6	7...10	> 30	> 30	> 30	> 30	> 30

NOTE: For alloy calibrations an optimum suite of traceable standards is available for each common type of alloy suitable to X-MET analysis.

In case of an identification model, the size of the identification library depends only on the needs of the particular application. The libraries altogether can hold data for as many as 400 reference samples.

4.5.3 Calibration sample selection

The samples are to be selected so that both the element and the concentration range in question are covered. In addition, the concentrations should vary in a way similar to figure 4.1.

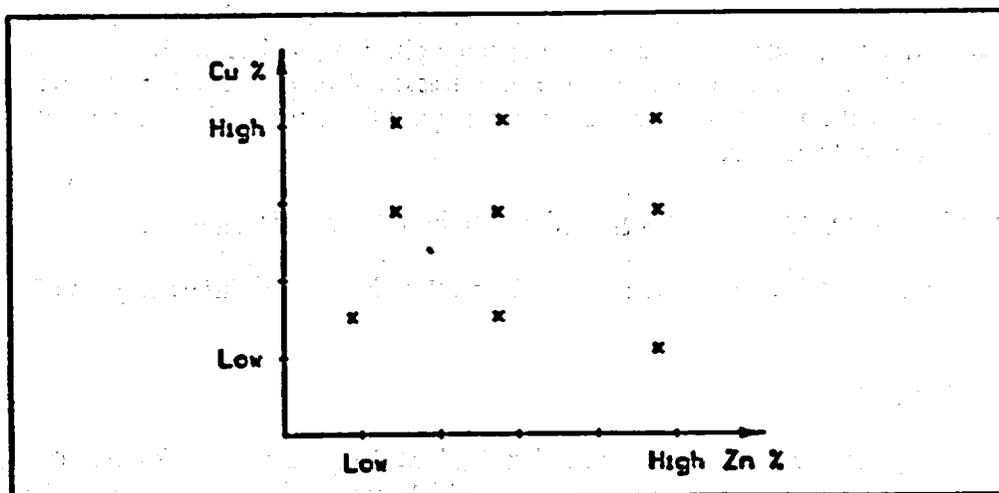


Figure 4.1 Example of ideal calibration sample concentration variation (for two elements).

If more elements are to be analyzed, a similar variation should occur between each element present in considerable quantities in the sample. A considerable quantity is over 10 % of the amount of the analyte (e.g. Mn) for a neighbouring, interfering element (e.g. Fe). Otherwise, it is simply a major component in the sample, which probably can affect the analyte's fluorescent radiation either by absorbing it, or by enhancing it. Notice also, that if an element of no direct interest is present in high concentrations, its variations should be included in the calibration sample series. Its matrix effects can then be accounted for in the calibration, which results in a more reliable model. In mining, metallurgical and hazardous waste applications, for instance, Fe is often such an element. Note that this applies mainly for the elements within the range of the probe -e.g. Si variations are less important in mining samples, when analyzing for heavier elements with a HEPS probe.

The powder or liquid sample quantity required by the X-MET is 10-20 grams. The powder samples should be ground and carefully mixed, i.e. homogenous. The recommended grain size for heavy elements is over 50 % being $\leq 74 \mu\text{m}$ (- 200 mesh). For measurements with the light-element probe, the recommended grain size is $\leq 20 \mu\text{m}$ (- 325 mesh).

Solid sheet samples $\geq (20 \times 20 \text{ mm})$ are suitable for a surface probe. For a measurement with a sample cup probe, samples should be less than 40 mm in diameter and 30 mm in height. The surface of the sample should be clean and preferably smooth ($< 50 \mu\text{m}$ roughness), smoothness is especially important with the light element probe (LEPS and SLPS) samples.

NOTE: The SAPS and DOPS probes can be equipped with a slit window for narrow objects, e.g. pipes.

Ensure before measurement that the samples have not changed chemically (e.g. oxidized). Crystallization in solutions can usually be redissolved by heating. Recrystallization must then be prevented during the measurement. All liquids should be clear without precipitating solids.

4.6. Sample cups and penetration of radiation

Powder and liquid samples are easily measured using special sample cups. The powder sample cup consists of a plastic cell, a snap-on ring and a plastic film. The liquid sample cup has a solid plastic top, and it is filled before the film is assembled. For volatile materials special sample cups with a vented cap are available, request these at your local representative, or from Outokumpu Instruments.

The foil must be replaced every time the sample in the cup is changed.

The appendix contains information on the chemical resistances of different types of films available.

Penetration depth

When filling the sample cup, the penetration depth of the primary radiation into the sample must be taken into account. Table D shows the layer thickness required for different substances to absorb 99 % of the primary radiation intensity. If the layer thickness of the material to be analyzed is smaller than the value in the table, either the mass or the volume of the sample must be standardized. This is normal for liquid and light-matrix powder samples measured with the heavy element probe HEPS, e.g. gasoline, mill tailings, silica sand, lubricating oils, etc. Normally filling the cup over half-height is enough.

Table D. Radiation penetration depths into different materials.

Source	Sample	Layer thickness mm
Fe - 55	Oil	3.0
	Quartz	0.1
Cm - 244	Oil	34
	Quartz	1.4
	Iron	0.04
Cd - 109	Quartz	4.8
	Iron	0.14
Am - 241	Quartz	40
	Copper	1.8

5. CALIBRATION OF THE ANALYZER

5.1 INTRODUCTION

5.1.1 General

The calibration procedure prepares the instrument for the tasks and applications determined by the user, and provides the data necessary for carrying out the measurements. The results acquired from the calibrations are stored in calibration blocks, models, which are associated with particular applications. Models can be assay models (sect. 5.3) or identification models (sect. 5.4). In certain cases intensity models are also used, e.g. to get information on composition variation.

In instrument calibration, there are two main points: 1) through the INI command, the probe is initialized for the gain control procedure to function in use; 2) pure element samples are measured through PUR command in order to set certain "windows" or channels for the elements of concern; also, through the BS, or backscatter sample the instrument is "taught" how to correct for the background in each element window. These spectra are stored in the X-MET memory, and they form the qualitative basis on which the actual measurements are founded.

Each of the 32 models available consists of up to ten element channels, BS included. The simplest possible application includes one element channel for the element to be analyzed, and a backscatter channel for the estimation of the background. Defining an identification model, however, requires always at least three pure element channels (2 + BS).

In the sample calibration of an assay model, a set of samples of known concentrations are measured, one by one, with the command CAL. Then the assay values of these samples for the elements of interest are entered with the command ASY. The actual modelling of the measured-vs.-entered data is done with the command MOD, where appropriate element intensities (independents) are chosen to make a mathematical model (measured intensities vs. assay values). In this way, a concentration-intensity -relation, (= formula, calibration curve) is calculated, thus making quantitative analysis possibly. See equations 2 and 3 in chapter 2, where the f_i 's are the independents.

In the case of an identification model, the calibration involves the measurement of a group of (identification) references that represent those to be identified in actual use. Their element concentrations need not be known, although it is mandatory to know in which elements (mainly) their composition differs (see section 5.4).

5.1.2 Calibration procedure

Before calibration measurements (or INI) are started, the instrument must be in the ON state with probe connected long enough to stabilize thermally and electronically. A stabilization time of 30 min. is sufficient, but after considerable changes in temperature a time of 30 min/20°C is necessary.

Calibration is divided into two parts: instrument calibration and sample calibration (figure 5.1). The instrument calibration includes gain control initialization (INI) and pure element cali-

bration (PUR) for a totally new probe, or a pure element calibration for a previously used probe. The sample calibration for assay models consists of calibration sample measurements (CAL), input of chemical assay values (ASY), and regression model calculations (MOD). In the case of an identification model, sample calibration consists only of reference sample naming and measurements (ADD).

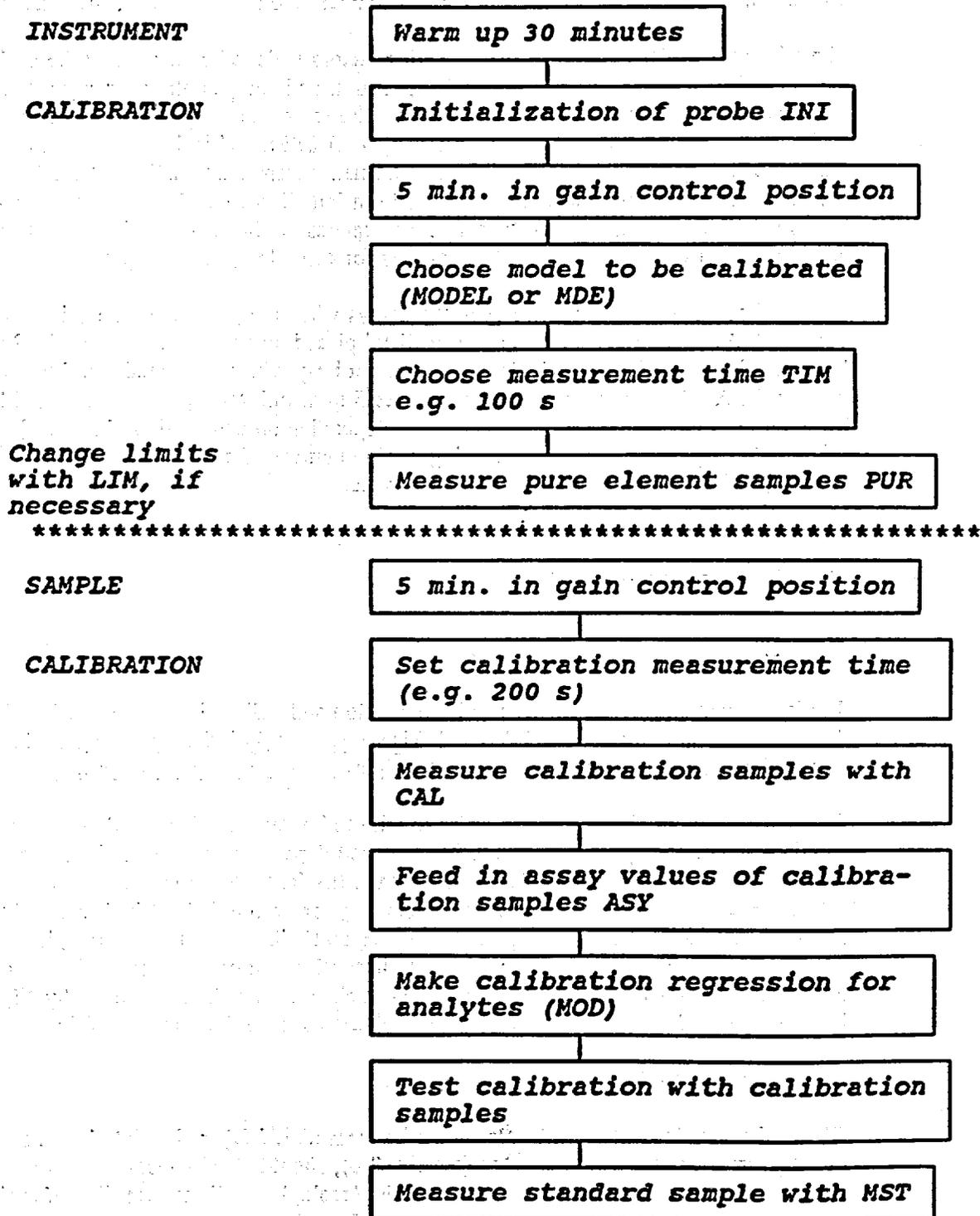


Figure 5.1 Calibration.

5.1.3 Gain control

The X-ray spectrum consists of a continuous distribution of X-ray quantum energies. The range of a source (probe) on the energy scale is divided into 256 microchannels. This energy-channel relationship is affected by several destabilizing factors such as temperature variations, variations in the properties of the electronic components, pressure etc. This means that a proportionally large error would result, if no compensation was made for these factors.

The elimination of the effects of these varying factors is done by monitoring the peak value of the internal gain control reference sample spectrum, and compensating for any movement of this peak on the microchannel (spectral) scale. The reference sample is located inside the probe shutter (or the probe cover, as in HEPS and LEPS), and is therefore accessible when the probe is in gain control position. The instrument automatically adjusts the gain value of the probe (preamplifier), once the probe has been initialized, i.e. the reference spectrum has been measured. The material of the reference depends on the source and source strength employed. In a word, the gain control corrects for drift along the energy scale.

The feedback gain control system operates always when the probe is in the gain control position (SAPS, DOPS trigger released or SLPS placed on its side, HEPS or LEPS with the lid in the front position) and the instrument is not busy with a command (the '>' prompt is displayed). A full gain control adjustment takes 5 min. uninterrupted. This should be allowed at least once each full hour (or more, depending on data quality objectives). Especially this should be performed when measuring a large number of calibration samples, when working under varying temperature conditions etc.

5.2 INSTRUMENT CALIBRATION

5.2.1 General

The instrument calibration consists of INItialization and PURe element calibration. INI is described in detail in section 4.2.3. Read this section first before proceeding. Perform INI only as instructed. INItialization is not necessary before every calibration.

Pure element calibration is done in order to tell the instrument where to find pulses for a certain element. The pure elements to be measured depend on the application. The idea is to measure, besides the analytes, elements, which will/might interfere with the analyte signal. Interference can be overlapping of a neighbouring, or even a $Z-2/Z+2$ element (check also for K / L -line interferences). Especially Z-1 element's K_{α} line can be overlapping element Z's K_{α} -line. Analyte signal enhancement / absorption can occur through elements with higher/lower characteristic energies: e.g. Fe can absorb the radiation emitted by Ni, resulting in a larger signal from Fe in the presence of Ni than e.g. in the presence of Ti.

What elements should be measured

Obviously, the elements of interest should be measured. Major elements in the sample, if in the measurement range of the source (see fig. 2.6), should also be measured. For example, Fe, Si and Ca are often such elements in mining/geological/soil samples, S and/or Cl in oil products, Ca in papers, Fe in steel applications. Interfering elements are mainly neighbouring or close elements to the elements of interest, causing overlapping of peaks, especially if in comparable concentrations. So, Z-1 and/or Z+1 elements should be included, as well as

Z-2 and Z+2 elements, if in relatively high concentrations. Also, elements upwards (with a higher characteristic energy) will leave a low energy tail (background), and may need to be included, if in relatively high concentrations. If analyzing for heavy elements in liquid samples with Cm, Cd or Am sources, include also Zn as pure element due to probe structure interferences (Zn-alloy).

5.2.2 Selection of model to be calibrated (MODEL, MDE - DEL)

The calibration begins by choosing the number of the model to be calibrated. The current model is displayed on the upper right corner of the LC display. It can be altered by pressing the MODEL key. If a new, uncalibrated model is selected,

UNCALIBRATED MODEL

is displayed. The model is now ready for calibration. Another way to choose a model is to use the command MDE.

If an old model is to be deleted, it can be done by using the command DEL. The instrument prompts for the number of the model to be deleted.

5.2.3 Selection of calibration measurement time (M.TIME, TIM)

Measurement time is displayed on the lower right corner of the LC display. It can be altered by pressing the M.TIME key, or through the command TIM. The current measurement time is displayed, and a prompt asks for a new one. The time is displayed in seconds. Pressing the CONT/YES key retains the current measurement time.

In PUR, a measurement time of 100 to 200 seconds is recommended. When significant overlapping is present, measurement times of 200 seconds is necessary.

5.2.4 Pure element calibration (PUR)

In the pure element calibration process the user sets "windows" for certain elements (element channels). The pure element samples (1-9 elements), and the backscatter sample can be measured in any order. The elements selected for an assay model should include all the elements of interest plus any elements that might interfere with them, either by a spectral overlap or by causing a matrix effect. The choice of elements for an identification model should include a minimum number of elements essential to differentiate between reference samples. However, at least two element channels + BS are needed in an identification model.

The analyzer stores the measured pure element data in the current model, and in a pure element table. It computes the correct microchannel limits for each element. All pulses falling between these limits are summed and calculated as total net counts of the respective element. The channel limits can be inspected and changed after pure element calibration using the command LIM. The analyzer calculates and stores also information acquired from the pure element measurements for the spectrum purification (deconvolution) calculations. This data manifests itself as the G-MATRIX (spectral overlap correction factors) under EMP/PRM command.

The instrument can store 20 pure element spectra in a separate table. They can be recalled conveniently from there for new models, without remeasuring them. The pure element spectra "age" while stored in the instrument, and must not be used if older than the normalization interval stated in sect. 5.5.1, e.g. no more than 2 weeks with Cd-109 source. Pure elements cannot be normalized, unless in models. When later calibrating a model, in the PUR sequence before the actual measurements, an inquiry DELETE OLD SPECTRA finds out whether you wish to erase the existing pure element spectrum table or not. It does not affect pure element spectra in existing models.

A unique name is given for a new model. Next, the instrument prompts for the first element. The elements are identified either by the element symbol, e.g. FE, or by a number. The symbol for the backscatter sample must always be BS.

Having entered the name and placed the pure element sample and locator ring inside the probe, push the probe into measurement position, and start the measurement by pressing the START key or by pulling the trigger of the surface probes. When the measurement is completed, the spectrum peak channel and the full width at half maximum height (FWHM) of the peak are displayed, and the instrument is ready for the second element. Pure element calibration can be terminated at any point with the END/NO key.

If the error message:

COUNT RATE TOO HIGH: 11 556
CONTINUE?

appears, this tells the user, that too great a pulse rate comes from the current sample. The easiest way to overcome this is by using suitable supplied limiter ring (Cu for the Fe-55 source, Al for the other sources), which limits the "visible" area of the sample. As the detector has an ideal range of operation up to 6000 c/s, this value should preferably not be exceeded. If a limiter is used in the pure element calibration, a note should be made of the size of the limiter, as this may be needed in the future if normalizing the model with this pure element.

Here is an example on the pure element calibration of a new model. Ni, Fe, Cr, Cu, Mo and backscatter channels are created.

```
> PUR
CALIBRATING A NEW MODEL
NAME: NI ALLOYS (max 16 characters)
1. PURE SAMPLE: FE4 (probe number 4)
MEASURE FE4 START
MEASURING: PROBE 4 TYPE SAPS
120 SECONDS LEFT...
PEAK CHANNEL: 90 FWHM: 14

2. PURE SAMPLE: CU
MEASURE CU4 START
MEASURING: PROBE 4 TYPE SAPS
120 SECONDS LEFT...
PEAK CHANNEL: 120 FWHM: 16

3. PURE SAMPLE: BS
MEASURE BS4 START
```

MEASURING: PROBE 4 TYPE SAPS
 120 SECONDS LEFT...
 PEAK CHANNEL: 255 FWHM: 1

4. PURE SAMPLE: CR
 MEASURE CR4 START
 MEASURING: PROBE 4 TYPE SAPS
 120 SECONDS LEFT...
 PEAK CHANNEL: 79 FWHM: 13

5. PURE SAMPLE: NI
 MEASURE NI4 START
 MEASURING: PROBE 4 TYPE SAPS
 120 SECONDS LEFT...
 PEAK CHANNEL: 109 FWHM: 15

6. PURE SAMPLE: END/NO
 CALIBRATION FINISHED
 >

We forgot to measure the Mo pure element sample also. We will give command PUR again:

> PUR
 DELETE OLD SPECTRA ? END/NO (If aged spectra, then delete)
 MODIFY ELEMENTS ? CONT/YES
 NEW MEASUREMENT FE4 ? END/NO (If CONT/YES is given, a
 NEW MEASUREMENT CU4 ? END/NO new measurement is needed
 NEW MEASUREMENT BS4 ? END/NO to replace the old spectrum)
 NEW MEASUREMENT CR4 ? END/NO
 NEW MEASUREMENT NI4 ? END/NO
 6. PURE SAMPLE: MO
 MEASURE MO4 START
 MEASURING: PROBE 4 TYPE HEPS
 120 SECONDS LEFT...
 PEAK CHANNEL: 220 FWHM: 18
 7. PURE SAMPLE: END/NO
 CALIBRATION FINISHED
 >

Switching between models is done with the MODEL key. Single pure sample spectra can be re-measured if necessary. Entering '-' for the NEW MEASUREMENT? prompt deletes the element in question from the current model. A CONT/YES deletes the spectrum from the pure element table also, and the instrument prompts for a new measurement for that element.

The pure element spectra in memory are accessible during pure element calibration. A pure element can be recalled from the memory by giving the element abbreviation in e.g. 2. PURE SAMPLE: FE4. If in the memory, the instrument prompts NEW MEASUREMENT FE4 ?, and if answered with an END/NO, the spectrum is recalled from the table. When the instrument calibration of a given model is completed, all the necessary information is stored in that model and the model no longer needs to refer to the spectrum table. Therefore the limitation of the spectrum table to 20 single element spectra does not limit the X-MET 880 to the

measurement of only 20 elements. If more than 20 spectra are added the first ones will be overwritten in the table. They are not overwritten from models, however.

5.2.5 Calibrating a model for several probes

An analysis task may require more than one probe/source combination to cover all the elements to be measured. In that case, a distribution box is necessary (sect. 3.10).

Proper care must be taken, so that all probes are allowed a sufficient stabilization time. At least 5 minutes should be allowed for each probe for gain control. The basic idea is to give the number of the probe after the element symbol in PUR, as was done in the previous example. When an element is measured with another probe, simply give the element symbol followed by the number of that probe: e.g. Fe4, Ni4, Mo4, BS4, Ag1, BS1, Si2, S2, BS2 (a model for probes 4, 1 and 2). A recalculation of a several-probe model cannot be made in another model, except for the last measured probe (source).

In sample calibration, X-MET will then prompt for the different probes by the probe number.

NOTE: Each probe requires its own BS sample; furthermore, all the pure elements must fit into the 10 allowed pure element channels.

5.2.6 DOPS pure element calibration

The DOPS pure element calibration is in principle the same as for other probes. An element should be designated in addition with the appropriate source letter, A or B, as in CR4A, CR4B BS1A, BS1B etc. In DOPS, the A source is the one with the higher energy. Also, backscatter (BS) samples should be measured with both sources, if the model is for two sources. The main difference, however, comes from the checking and possible setting of limits for the B source pure elements and BS. This is because the spectrum is compressed for the B source, and the backscatter peak is approx. in channel 130...140 for the B-source. If the BS is the highest peak, the instrument takes it as a pure element peak. This happens especially with the Fe-55 source when measuring e.g. a 2% Ti pure element sample. The solution is to print out the spectra with SPL (or check with SPE), and find the limits corresponding to the half-maximum width of the desired peak, and then set the limits accordingly with the LIM command. Do not let limits for neighbouring elements overlap each other, otherwise a warning **OVERLAPPING LIMITS** will appear. Also, one must take into account possibly overlapping elements separately for each source. Thus, e.g. in a Fe-55/Cd-109 DOPS, Ti and Cr must be measured with both sources in stainless steel or other alloy applications. These elements will appear in totally different channels for each source, which is quite normal.

Note also, that as only one spectrum can be stored in the instrument memory, a recalculation of a measurement made with both sources is not possible.

5.2.7 Examining pure element spectra (SPE)

If the channel limits set by the automatic setting are to be altered (with LIM command), it will be necessary first to examine the pure element spectra in question. SPE performs this. SPE will output the channel counts of the last measured spectrum, or a chosen pure element spectrum.

If the same pure element has been measured with several probes, the instrument will also prompt for the probe number. After that, microchannel numbers and the corresponding number of pulses accumulated in that microchannel can be viewed. Press CONT/YES and Δ keys to scroll forward and backward. Entering a slash "/" and a number between 0 and 255 results in the corresponding channel being displayed. As usual, pressing the END/NO key terminates the viewing.

```

> SPE
LATEST ?                               END/NO
14 PURE ELEMENT SPECTRA                (List of pure elements to printer/terminal)
WHICH OF THEM ?   FE
WHICH PROBE ?     4                    (If several Fe spectra exist in memory)

0:      35
1:      0
2:      0      /70      CONT/YES
70:     120
71:     125
.
.
255:    12654          END/NO
>

```

5.2.8 Spectrum plot using an external printer (SPL)

If a printer or a data terminal is available, the spectrum/spectra in the X-MET memory can be plotted with the command SPL. Spectrum selection is similar to that of the SPE command.

X-MET allows the output to be formatted in several ways. Altering the microchannel (First channel - last channel) and pulse count limits (range lower - range upper), it is possible to focus on any part of a spectrum. The default values can be accepted by simply pressing CONT/YES. WINDOW stands for the number of adjacent microchannels displayed as a single bar, therefore defining the printout resolution: WINDOW 1 means that every microchannel is displayed, WINDOW 3 means that 3 channel counts are added together and every 3rd channel is displayed, with the integrated total.

Example 5.2 shows a typical spectrum printout. The spectrum is a Si pure element sample measured on LEPS probe, a Fe-55 740 MBq source and a 15 s measurement time. The dimensions are not quite correct: the actual printout is full 80 characters wide. The numbers on the left are the microchannel number and the corresponding amount of pulses in it. Notice the use of a WINDOW 5 produces a more compact listing.

Note, that the graph is an uncorrected spectrum, i.e. from the measured pulses, and not from the intensities. The peak of an analyte may not even be visible on the spectrum, and still we can have totally reliable results.

Example of a spectrum printout:

```

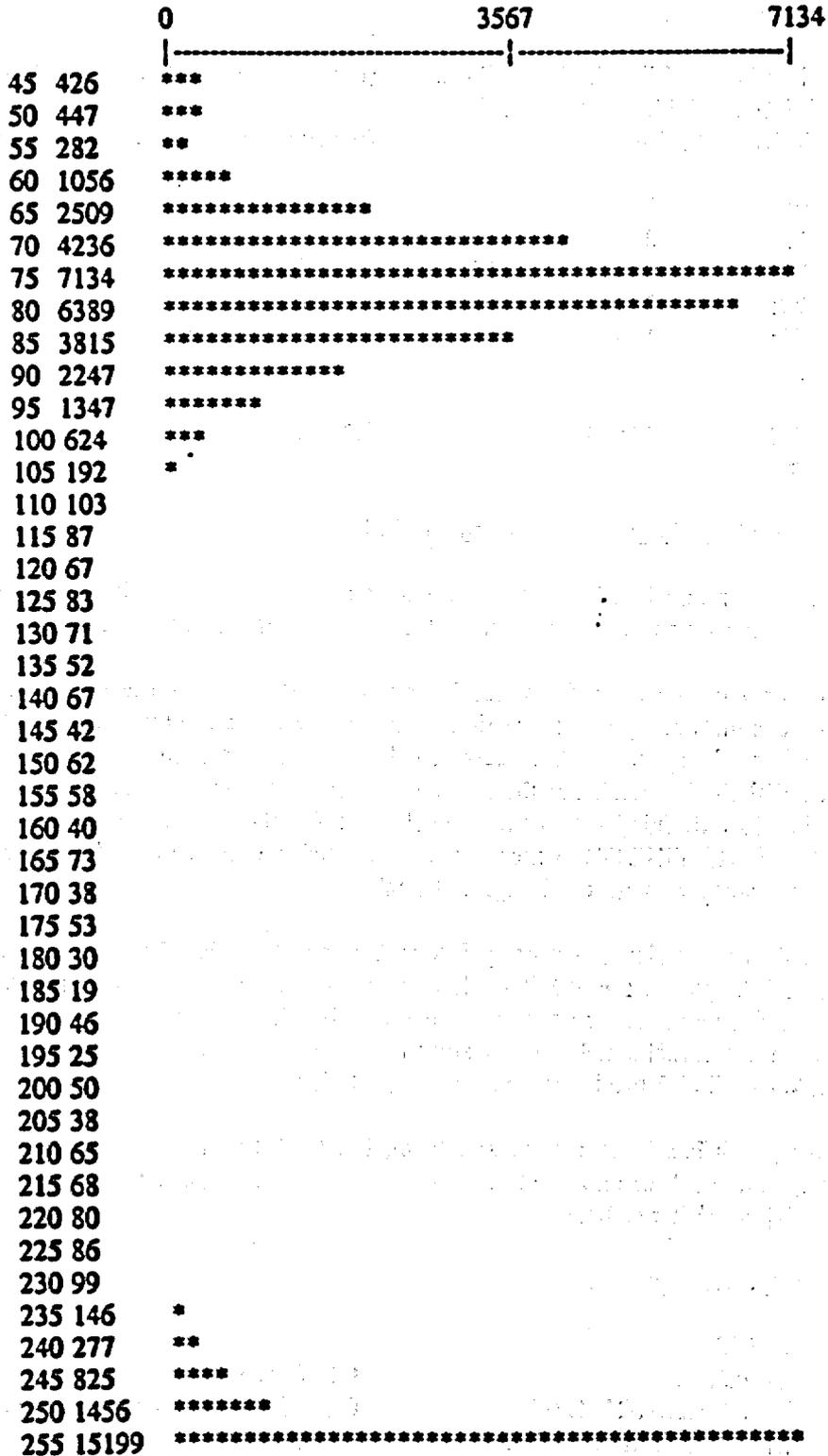
> SPL
LATEST?                               CONT/YES
FIRST CHANNEL 0 ? 45                  CONT/YES (Starts from microch. 45)
LAST CHANNEL 255 ?                   CONT/YES

```

WINDOW 1 ? 5
RANGE, LOWER 0 ?
RANGE, UPPER 7134 ?

CONT/YES (Prints every 5th channel)
CONT/YES (Scaling, if necessary)
CONT/YES

**** LATEST SPECTRUM MEAS.TIME: 15 DATE: 17.01.91 12-09-34



NOTE ! If command PUR is given after the limits have been changed, they will change back to their original values.

5.2.10. Pure element calibration step-by-step

- 1) Let the instrument stabilize for 30 min. with the probe in gain control position.
- 2) Do INItialization for probe, only if not done before. Keep record of probe number. Choose manual normalization.
- 3) Let each probe stabilize at least 5 min. in gain control position.
- 4) Choose model with MODEL key. DELete old model, if necessary.
- 5) Set measurement time to min. 100 s with M.TIME key, or TIM command.
- 6) Measure pure elements with PUR command. If count rates over 6000 c/s occur (COUNT RATE TOO HIGH), use limiter. Make a note which limiter is used for each element. Do not forget the BS sample.
- 7) If still with smallest limiter COUNT RATE TOO HIGH, then change maximum count rate from default 6000 to 10 000 with command EMP/PRM-GENERAL PARAMETERS-Max.-count rate by giving END/NO to default 6 kHz, and changing it to 10 kHz. Accept with CONT/YES, press END/NO, until prompt > appears.
- 8) Change LIMits, if necessary (normally not). Check that element limits are in an order related to energy. BS should be in channel 255.
- 9) Plot spectrum of BS sample, if possible, to check for impurities (not necessary, if a pure element sample is used as BS).

NOTE ! The pure elements cannot be measured or modified after calibration samples (CAL,-ADD) have been measured. Doing this will cause erroneous results. To recover, delete added pure elements, or make a new sample calibration (CAL).

5.3 CALIBRATION OF AN ASSAY MODEL

5.3.1 Introduction

When the instrument calibration of the analyzer has been completed, the analyzer is capable of computing the net counts (intensities) in an element channel. In order to proceed to concentrations or identification results, sample calibration is required. This involves the measurement of a set of known samples, with the same physical form as the real samples have (powders, liquids, solids).

For sample calibration of an assay model, calibration samples are measured one after the other using CAL, then the reference assays of these samples are entered in with the command ASY, and the assay model is generated with regression analysis, through command MOD. The calculations can be performed either internally, using the analyzer software with a maximum of 30 samples, or externally, in which case there are no restrictions to the number of samples. See ch. 4 for calibration sample selection.

The concentration data of the calibration samples has to be from a reliable, independent method of analysis, e.g. wet chemical analysis, WDXRF, AAS, ICP: Best correlation is normally achieved with WDXRF data. The accuracy of these analyses defines the achievable maximum accuracy of the later X-MET analyses.

For sample calibration of an ID model, see section 5.4.

5.3.2 Sample calibration of an assay model (CAL)

In the sample calibration of an assay model, the X-MET stores the intensities of the measured calibration samples in a calibration table. There they can be read or altered (CIN), or used as a basis for a regression model calculated by the X-MET regression program (MOD). The calibration table is common to all models. The instrument cannot store more than the data needed for one model at a time. Consequently, only one model can be manipulated at a time. Once a calibration data set (intensities & concentrations) is deleted, the regression calculations (MOD) cannot be performed for that set unless the data is fed in again. The practical implication is that the user should finish the making of an assay model before starting a new one with CAL. A command PUR or ADD in another model will not interfere with, or destroy, calibration data.

The maximum size of the calibration table is 30 samples: should there be a need for a larger amount of calibration samples, the calculations of the regression model will have to be performed externally. The calibration samples can be measured in an arbitrary order. (Be sure, however, to make a record of this order.) The calibration table recognizes the samples by numbers (1-30) only.

Before command CAL is executed, it is advised to check the total count rate TCR of the most concentrated sample. This in order to see if a limiter is needed or not. If a limiter is needed, it must be used with all the samples, and it must be of the same size throughout the measurements.

As command CAL is executed, the user is given information about the status of the calibration table, such as:

```
NO OLD DATA , MEASURE SAMPLE 1 or
OLD DATA: 30 SAMPLES (TABLE FULL) or
OLD DATA: nn SAMPLES MODEL xx
OVERWRITE?
```

If calibration data from previous calibrations is to be used (e.g. MODelling not finished), a negative reply (END/NO) should be entered after the OVERWRITE prompt. If the previous model is finished, a positive reply erases the calibration table and allows a new model to be started.

The X-MET prompts for one sample at a time:

```
MEASURE SAMPLE nn
```

The following replies are possible: i) START measures the sample, ii) number mm proceeds to sample number mm, and iii) END/NO terminates the sample calibration.

NOTE: A useful point is the ability to use the spectrum of a calibration sample already measured also as an identification model reference. This can be done for the latest sample that has been measured. Terminate CAL, start ADD (sect. 5.4.1), and reply to 5. REF. SAMPLE prompt with the name of the reference, followed by the CONT/YES and then the RECALC key. The result of the latest calibration sample measurement is stored as the fifth reference. This works also the other way, from ID to assay model.

Thus you can use a calibration sample measurement as an identification model reference and as an assay model calibration sample without remeasuring.

Samples can be entered in an arbitrary order. The same sample can be measured several times, if necessary. After END/NO, the storing of the samples is confirmed:

LAST SAMPLE nn?

At this point it is possible to leave out the last samples, beginning from number nn. The reply entered can be the number of the last sample to be stored; samples numerically after it will be deleted. The default value is to store all samples, by replying CONT/YES.

Once the thirtieth sample is measured, the calibration table capacity limit is reached and a message TABLE FULL is displayed. It is, however, possible to continue the calibration, if first the intensities for the first 30 calibration sample values are recorded (CIN). After this, the following samples will overwrite the last sample in the calibration table. However, the calibration calculations have to be carried out externally.

5.3.3 Examining calibration intensities (CIN)

The measured calibration sample intensities can be read or altered using the CIN command. The printout can then be used for generating regression models externally. This is compulsory, if the number of calibration samples exceeds 30. The display shows first the number of calibration samples and element channels. After that it is possible to scan the intensities.

CONT/YES and Δ keys scroll forwards and backward. Numerical data typed is taken to be a new value for the displayed intensity. A slash (/) followed by a number proceeds to that sample. P + CONT/YES sends the intensities in a table form to an external printer or terminal, when at an intensity line.

Example:

```
> CIN
11 * 5 INTENSITIES

1. SAMPLE NI: 1964.0000? P      (output to printer/terminal as a table)
.
.                               CONT/YES
1. SAMPLE FE: 1234.0000? 1536
1. SAMPLE FE: 1536.0000?      CONT/YES
1. SAMPLE CR: 21.9100? /11    (go to sample no. 11)
11. SAMPLE FE: 1307.0000? etc. END/NO
>
```

Display shows the number of the sample, the name of the element channel and the intensity of that channel. A very good reason must exist in order to change the measured intensities. Normally, this is not advisable.

5.3.4 Entering the assay values (ASY)

Command ASY is used to enter the calibration sample element concentrations. It prompts first

for the elements of interest, the dependents. These are the elements to be analysed for. The concentration data is entered after the question mark prompt. As usual, CONT/YES retains the previous value, and END/NO terminates the command. A P + CONT/YES after any concentration value line gives an output in table form to printer/terminal. Example:

```

> ASY          CONT/YES
OLD DEPENDENTS:
NEW: PB ZN FE  CONT/YES
NEW DEPENDENTS: PB ZN FE ?          CONT/YES
1. SAMPLE PB: 0.000 ? 2.3          CONT/YES
1. SAMPLE ZN: 0.000 ? 11.4         CONT/YES
1. SAMPLE FE: 0.000 ? 24.5         CONT/YES
2. SAMPLE PB: 0.000 ? 3.4          CONT/YES
2. SAMPLE ZN: 0.000 ? etc.
.
.
15. SAMPLE FE: 0.000 ? 14.5        CONT/YES
15 * 3 SAMPLES
>

```

To check the entered values it is strongly recommended to go through the samples one by one. Jumping from one sample to another in the table can be accomplished by giving a slash (/) and the sample number:

```

> ASY          CONT/YES
OLD DEPENDENTS: PB ZN FE
NEW :          CONT/YES (if an element is to be added
               or removed, give new elements)
1. SAMPLE PB: 2.3 ? P             CONT/YES (to get a printout in table
.                                   form)
.                                   CONT/YES
1. SAMPLE ZN: 11.4 ? /12          CONT/YES (proceed to sample 12)
12.SAMPLE PB: 3.7 ? 3.2          CONT/YES (correction of a typing error)
12.SAMPLE ZN: 13.8 ?             END/NO
15 * 3 SAMPLES
>

```

In this way incorrect entries can easily be corrected.

5.3.5 Generating the regression curve (MOD)

Command MOD starts the multiparameter regression calculation program. The first selection is the choice of the dependent on which the regression is to be performed (REGRESSION FOR FE ?), i.e. for the first analyte. Second selection is for the independents, those elements that have effect on the fluorescent radiation of the dependent and which are included in the regression calculations.

The independents can be specified either by the element symbol or element number (as defined in PUR). The permissible independent combination syntaxes and their meanings are as follows (refer to sect. 2.14):

Form entered to X-MET Mathematical meaning

FE		(element intensity)
FE/	= FE/BS	(elem. intensity divided with backscatter)
FE*BS		
BS		(backscatter intensity)
BS/	= 1/BS	(reciprocal of BS intensity)
FE*FE		(element intensity squared)
FE*CR		(product of two element intensities)
FE*CR/	= FE*CR/(BS*BS)	
FE*BS/	= FE/(BS*BS)	
BS*BS/	= 1/(BS*BS)	(reciprocal of BS squared)

All elements entered in PUR are allowed, including BS. If an element is measured with several probes, the appropriate probe number should be used (and is prompted for), e.g. CA2, CA5. Note, that in several probe models independents measured with one probe can be used as independents for an element measured with another probe.

Pressing the END/NO key quits independent selection, and initiates the calculation. Should the chosen independents include elements that have not been used in calibration, an error message USE: [available elements from pure element calibration] is displayed, and the selection must be carried out again.

The main guidelines of calibration are as follows:

- 1) Start regression with the analyte as the first independent (i.e. dependent = 1. indep)
- 2) Minimize model error S, with a t-value higher than |2.5| for every independent
- 3) The chosen independents should be as simple (in form) as possible. The simplest form is e.g. Fe (element intensity), then Fe/BS or Fe*BS, then Fe*Fe, then Fe*Cr (or 1/(BS*BS)), then Fe/(BS*BS), then Fe*Cr/(BS*BS), which is the most complex variable. The better the sample space is covered (a large number of samples), the more complex variables can be used.
- 4) Check, that you do not overcorrect the model: if the model S value is smaller than the STD for the same element, then you have mathematically overcorrected the model, and it will not work properly. The STD should be about 10...50 % of the S value.

Example:

```

> MOD
REGRESSION FOR CU ?      CONT/YES
Stop indep input with END key
1. indep ?  CU          CONT/YES
2. indep ?                END/NO

```

```

R = 0.968  S = 0.583  F(1,13) = 75.4
RESIDUALS ?

```

After the internal regression calculation, the following parameters are displayed:

- R = correlation coefficient between assay and estimate values
 S = average regression (curve) error at midpoint of range; to be minimized
 F (M, N) = F-test value of regression with degrees of freedom M, N.
 M = number of independents
 N = number of samples - (M+1)

The next inquiry concerns the examining of the residuals (i.e. the comparison of the reference concentrations and those calculated by the model). CONT/YES brings the residuals on the display, END/NO passes this option. The notation is as follows:

- ASSAY = reference concentrations (those entered with ASY)
 ESTIM = conc. estimated (calculated) by model
 RESID = ASSAY - ESTIM
 ST.RES = RESID / S (a point's distance from the calibration line in number of standard RMS errors, e.g. 1.254 is 1.254 x S away from the line).

Example of a residual readout:

RESIDUALS ?	CONT/YES			
NO	ASSAY	ESTIM	RESID	ST.RES
1	30.300	29.875	0.425	0.274

Once again, CONT/YES and Δ keys are used for scrolling, and END/NO key for termination. If an external printer or terminal is connected, P CONT/YES produces output in table form and D CONT/YES as a calibration plot diagram.

The next inquiry is

DELETE POINTS :

At this point it is possible to leave some poorly fitting data points out of the regression model calculations. Possible reply could be 3 5 (separated by a space), which leaves samples 3 and 5 out of the regression calculations, which is automatically done again, and the corresponding new R, S and F values are calculated. The deleted points are not shown on the table. If a printout is made in table form of the residuals, the instrument renumbers the points with a running number, a fact that should be remembered, if more points are to be removed (find the number of the point to be removed in the printout for a full data set). The removed points are automatically recovered, if the iteration is begun again (choosing independents).

A poorly fitting point should not be deleted right away: this point may be subject to matrix effects, and it may turn out to fit a curve perfectly with a correct combination of independents. Only after several iterations have been made trying out several combinations of independents, a point with a poor fit in most every combination can be deleted. Usually, if the standard residual (st.res) in the table is larger than ± 2.000 , the point may be an erroneous point, and it should be noted. First, a remeasurement of that sample should be made in CAL, and then observed, whether the point still has a poor fitting. If so, then it can be deleted. Points with the lowest or highest concentrations should be allowed higher st.res. values.

Next prompt is for the display of

COEFFICIENTS AND T-VALUES?

This provides statistical test data about the independents involved in the regression calculations (for a full description of the t-test, refer to sect. 5.3.7). Each independent has its associated t-value: a high t-value (larger than ± 2.5) means generally a good independent, and a small t-value a poor independent, which should be deleted or replaced with another one.

CHANGE INDEPENDENTS?

If the model created does not require changing, reply END/NO. The computed calibration parameters are stored into the model. After a CONT/YES reply, the selection of independents, computation, point editing and related procedures can be performed again and again until the user finds the resulting parameters satisfactory (iterative procedure).

Finally, an inquiry is made for a new dependent (REGRESSION FOR XX ?). END/NO terminates the command and returns to command level (prompt '>').

NOTE: Make a habit of recording the final calibration parameters for future use (indeps, intercept, slope values, S value, t-value).

5.3.6 Choosing independents into the model

The most important part of the modelling is choosing the correct independents, or variables, for the model. The method is plainly empirical: one has to try out different combinations of independents, and see which combination produces the best results. A few guidelines can be given (see also appendix: How to create the best possible assay model).

1) Try as the 1. indep first the element itself (for which the regression is made), then the element multiplied by the BS, then divided by the BS (i.e. independents Cu, Cu*BS, Cu/BS). Choose the one which gives the lowest S value, but the simplest one: an improvement of ca. 10...20 % is necessary to justify for a more complex variable (e.g. to justify use of Cu*BS instead of Cu). In cases of small concentrations of the analyte, also a cross product with some major element can be tried (e.g. Cu*Fe). The first indep should always contain the element in question.

2) As the second indep try all the pure elements as included in the PUR: also, try the analyte multiplied by itself (correction for self-absorption, especially with heavy elements like Pb). If the first indep is the element alone (e.g. Cu), try also here Cu*BS and Cu/BS. Choose the best one of these, i.e. the one, which gives the lowest S value on the condition of a high enough t-value, and which is the most simple, fulfilling the 10...20 % rule. Note the other elements giving good results, and which have high t-values.

3) Still as the second independent try cross products of the elements which had the best t-values. For example, we have Cu/ as the first, and we got good results with Fe, Zn and Pb. Now we shall try as the second independent Cu*Fe, Cu*Zn and Cu*Pb, and see, which of them gives the best result, remembering the t-value limits ± 2.5 and the 10...20 % improvement in S value.

4) We choose from the possibilities above the most simple variable as the second independent.

5) As the third independent, we shall try again all the pure elements, and make choices accordingly.

As a general rule, one should try to use as independent elements those, which have a large

variation in their calibration intensities. In modelling we are trying to find which element intensities correlate with the intensity of the analyte - the correlation can be either positive or negative. Obviously, elements which have correlating concentrations, should have also a correlation in their intensities. But here we see then the importance of a good coverage for all elements present in the calibration samples (range and increment): let us assume, that in some mineral sample two elements appear as a salt, e.g. NiS. Then we can find a good correlation (good t-values) between these two as independents in a model for Ni. However, if the mineral samples to be measured (actual samples) contain more of FeS than the calibration samples, the correction made with S to the model for Ni will cause erroneous results. Thus, it is of utmost importance that the calibration samples cover the variations of all (major) elements.

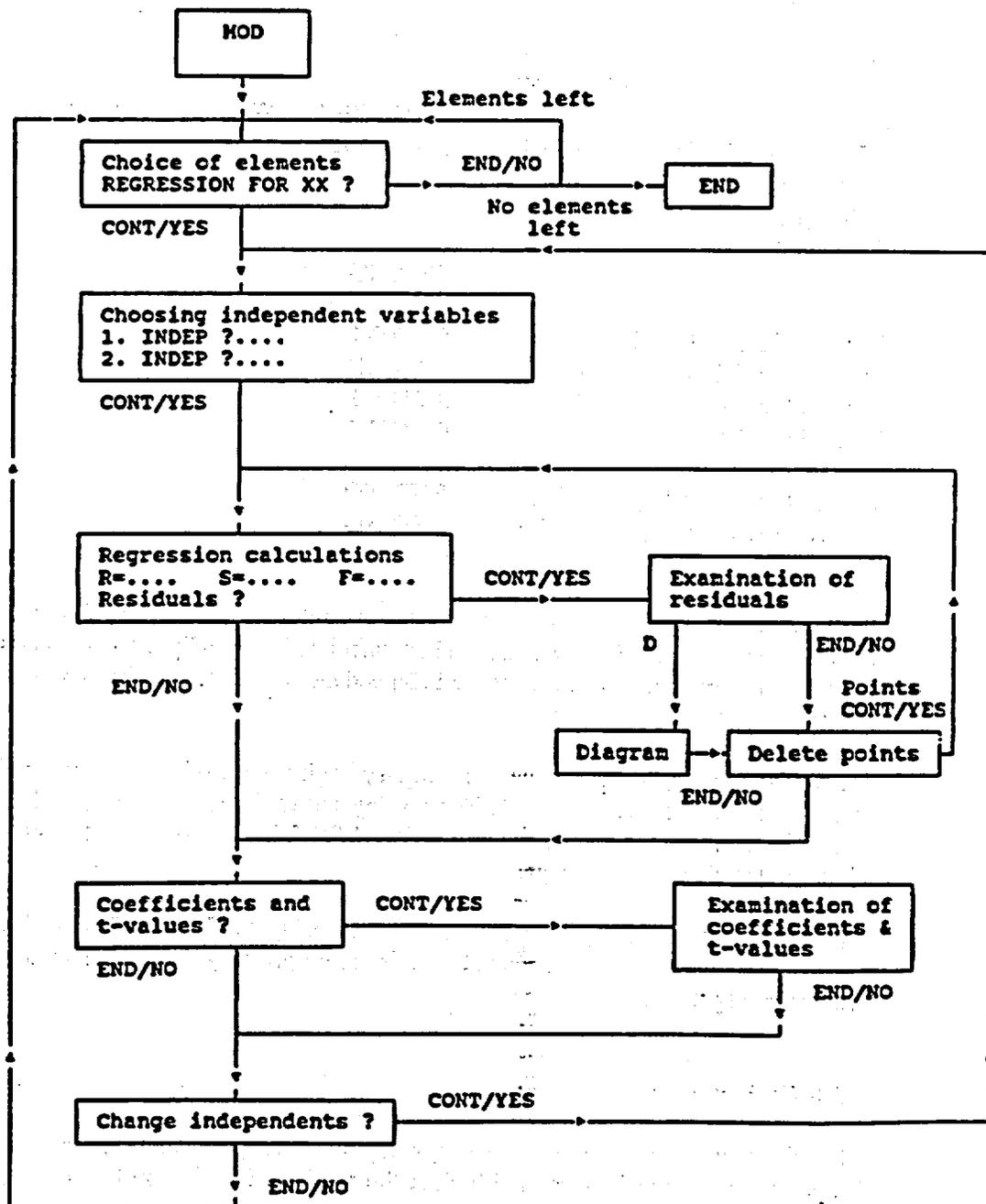


Figure 5.2 The flow chart of the command MOD.

5.3.7 Entering and changing the regression parameters (PAR)

When entering regression parameters from external calculations, or examining and possibly altering the regression parameters obtained from MOD calculations, the command PAR is used. The initial stages are similar to the MOD command; dependents and related independents are chosen similarly. Note, that in the PAR command the instrument does no calculations. The coefficients and intercept values, as well as the independents are used in concentration calculations of an actual measurement.

Example:

```

> PAR
OLD DEPENDENTS: FE CR NI
NEW:
FE-PARAMETERS (YES/NO) ?      CONT/YES (Write new ones, if necessary)
                                CONT/YES
1. indep ? FE
2. indep ? CR
3. indep ? NI
4. indep ?                      END/NO

INTERCEPT = 0.000E0          4.857E-1
SLOPE OF FE = 0.000E0          1.3664E1
SLOPE OF CR = 0.000E0          9.774E-2
SLOPE OF NI = 0.000E0          6.847E-4

CR-PARAMETERS (YES/NO) ?      END/NO
NI-PARAMETERS (YES/NO) ?      END/NO
>

```

In this example, we had measured calibration samples with CAL, and fed in the assays with ASY for Fe, Cr and Ni. However, we had calculated externally the parameters for Fe, and we entered them manually in: first the independent variables, and then corresponding intercept and slope values.

An END/NO reply to the independent inquiry begins the display phase (assuming that at least one independent has been chosen). The display shows the INTERCEPT and SLOPE values. The default values can be accepted with CONT/YES key, or replaced by entering new values after the question mark prompt.

The normal data scanning is available. As previously, P CONT/YES produces a table form output. Termination of the command is finished by pressing the END/NO key until the '>' prompt is displayed.

5.3.8 Calibration tests

After the sample calibration procedure, carry out measurements on a few standard samples. Measure one sample 5 times, and look at the average. Should you find the results inadequate, check the following items:

- whether the sample measured is of the type (matrix and elements) the model is calibrated for and concentrations are between calibration ranges

- * If checking a calibration sample, check that it was not deleted in MOD
- * the sample fit in the calibration line (residuals), if a calibration sample
- * whether the poor result is due to statistical variation
 - check with STD command, especially relative to model S values. Note, that the model S value is for the measurement time employed in CAL
 - increase the measurement time to increase precision
- * Check that model S value is not smaller than corresponding STD value
- * the data input to the models
 - check assay input values (ASY)
 - check the manually set limits (LIM)
 - check the coefficients of an externally computed model (PAR)
- * Check that all model indeps have t-values larger than 2.5 absolute
- * Check that neighbouring elements of analyte do not appear in concentration ratios smaller than 1:20...1:50
- * the instrument calibration (pure elements, BS sample)
- * the sample calibration (particle size, moisture, sample order, reference assays)
 - repeat if necessary.

Should you find all this appropriately done with no significant improvement in test results, contact a representative of Outokumpu Instruments.

5.3.9 Statistical tests of a regression model

This section discusses the interpretation of the two statistical tests included in the X-MET 880 software, that help the operator optimize the regression model for a given calibration.

Errors of measurement can generally be grouped into two classes, instrumental errors and those associated with the analyzed samples (calibration standards) and the measurement procedure itself. The sample related errors include sample placement, heterogeneity, particle size, surface condition, shape, preparation method, sample representativity, and the accuracy of the reference analyses of the calibration samples. For information on sample preparation and selection of standards see sect. 4.4.

The main sources of instrumental error of the X-MET 880 are:

- * counting statistics, i.e. too few pulses appear from target atoms as a result of a too short measurement time, or too small a concentration, or a weak or incorrect source
- * variation of primary radiation output intensity from source
- * electronical drift

Errors due to counting statistics, as well as the effects of drift, can be measured merely by repeated measurements of the sample (precision, repeatability). By comparing the average result and the standard deviation of 5-10 measurements to the STD of the model should give sufficient proof of the magnitude of the precision. Notice that the instrument gives a standard deviation based on counting statistics alone (STD), and is NOT a standard deviation of several measurements.

The X-MET analyzer is equipped with two useful tests for model judgement: the F-test and the t-test.

The F-test compares two kinds of variations: the variation of the sum of squares of the estimates calculated by the regression model, and the total sum of squares of the residuals (a residual is the difference between the measured concentration value and the given value for a known calibration sample). If F is larger than the critical value, the regression model being tested is probably a good one. Table E lists critical values for F, corresponding to a 95% confidence level, for various numbers of independent variables (m) and degrees of freedom (n). See also appendix for more information.

Examples of the effects of different regression models on the F-test value are shown in figures 5.3 and 5.4. Note the relation of the correlation coefficient R and the F-test value. An R-value approaching unity corresponds to a high F-test value in respect to the critical value.

Figure 5.3 illustrates simple (two-dimensional) cases of one dependent (x) against one independent variable (y). In 5.3a the residual variation around the model (the model is the straight line) is relatively large so the model is poor. In 5.3d the residual variation around the model is small and the model is good. 5.3b and 5.3c are intermediate cases.

Figure 5.4 shows some other examples. In 5.4a there are too few data points and the fit appears perfect, but from a practical point of view will not correctly represent the broader variations found in real life applications. The number of samples must be always larger than the number of model parameters (i.e. independent variables). In 5.4b the data points are clustered too closely resulting in an unreliable model. In 5.4c there is good correlation but not with the linear model chosen. In 5.4d the poor value of F is due to an incorrect data point (a possible typing error, or an erroneous reference analysis).

Table E. Critical values of the F-test for a 95 % confidence level.
 m = No. of independent variables
 n = No. of samples - (m + 1)

F-Distribution, Upper 5% Points [$F(\nu_1, \nu_2, 0.95)$]
 Degrees of Freedom for Numerator

5%

ν_2	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	161.4	199.5	215.7	224.6	230.2	234.0	236.8	238.9	240.5	241.9	243.9	245.9	248.0	249.1	250.1	251.1	252.2	253.3	254.3
2	18.51	19.00	19.16	19.25	19.30	19.33	19.35	19.37	19.38	19.40	19.41	19.43	19.45	19.45	19.46	19.47	19.48	19.49	19.50
3	10.13	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.74	8.70	8.66	8.64	8.62	8.59	8.57	8.55	8.53
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.77	5.75	5.72	5.69	5.66	5.63
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.53	4.50	4.46	4.43	4.40	4.36
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.84	3.81	3.77	3.74	3.70	3.67
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.57	3.51	3.44	3.41	3.38	3.34	3.30	3.27	3.23
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.12	3.08	3.04	3.01	2.97	2.93
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.90	2.86	2.83	2.79	2.75	2.71
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.85	2.77	2.74	2.70	2.66	2.62	2.58	2.54
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.61	2.57	2.53	2.49	2.45	2.40
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.51	2.47	2.43	2.38	2.34	2.30
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.42	2.38	2.34	2.30	2.25	2.21
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.35	2.31	2.27	2.22	2.18	2.13
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.29	2.25	2.20	2.16	2.11	2.07
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.24	2.19	2.15	2.11	2.06	2.01
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.19	2.15	2.10	2.06	2.01	1.96
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.15	2.11	2.06	2.02	1.97	1.92
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.11	2.07	2.03	1.98	1.93	1.88
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.08	2.04	1.99	1.95	1.90	1.84
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.25	2.18	2.10	2.05	2.01	1.96	1.92	1.87	1.81
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.23	2.15	2.07	2.03	1.98	1.94	1.89	1.84	1.78
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.20	2.13	2.05	2.01	1.96	1.91	1.86	1.81	1.76
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.18	2.11	2.03	1.98	1.94	1.89	1.84	1.79	1.73
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.16	2.09	2.01	1.96	1.92	1.87	1.82	1.77	1.71
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27	2.22	2.15	2.07	1.99	1.95	1.90	1.85	1.80	1.75	1.69
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25	2.20	2.13	2.06	1.97	1.93	1.88	1.84	1.79	1.73	1.67
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24	2.19	2.12	2.04	1.96	1.91	1.87	1.82	1.77	1.71	1.65
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22	2.18	2.10	2.03	1.94	1.90	1.85	1.81	1.75	1.70	1.64
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.89	1.84	1.79	1.74	1.68	1.62
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.00	1.92	1.84	1.79	1.74	1.69	1.64	1.58	1.51
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.92	1.84	1.75	1.70	1.65	1.59	1.53	1.47	1.39
120	3.92	3.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96	1.91	1.83	1.75	1.66	1.61	1.55	1.50	1.43	1.35	1.25
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.52	1.46	1.39	1.32	1.22	1.00

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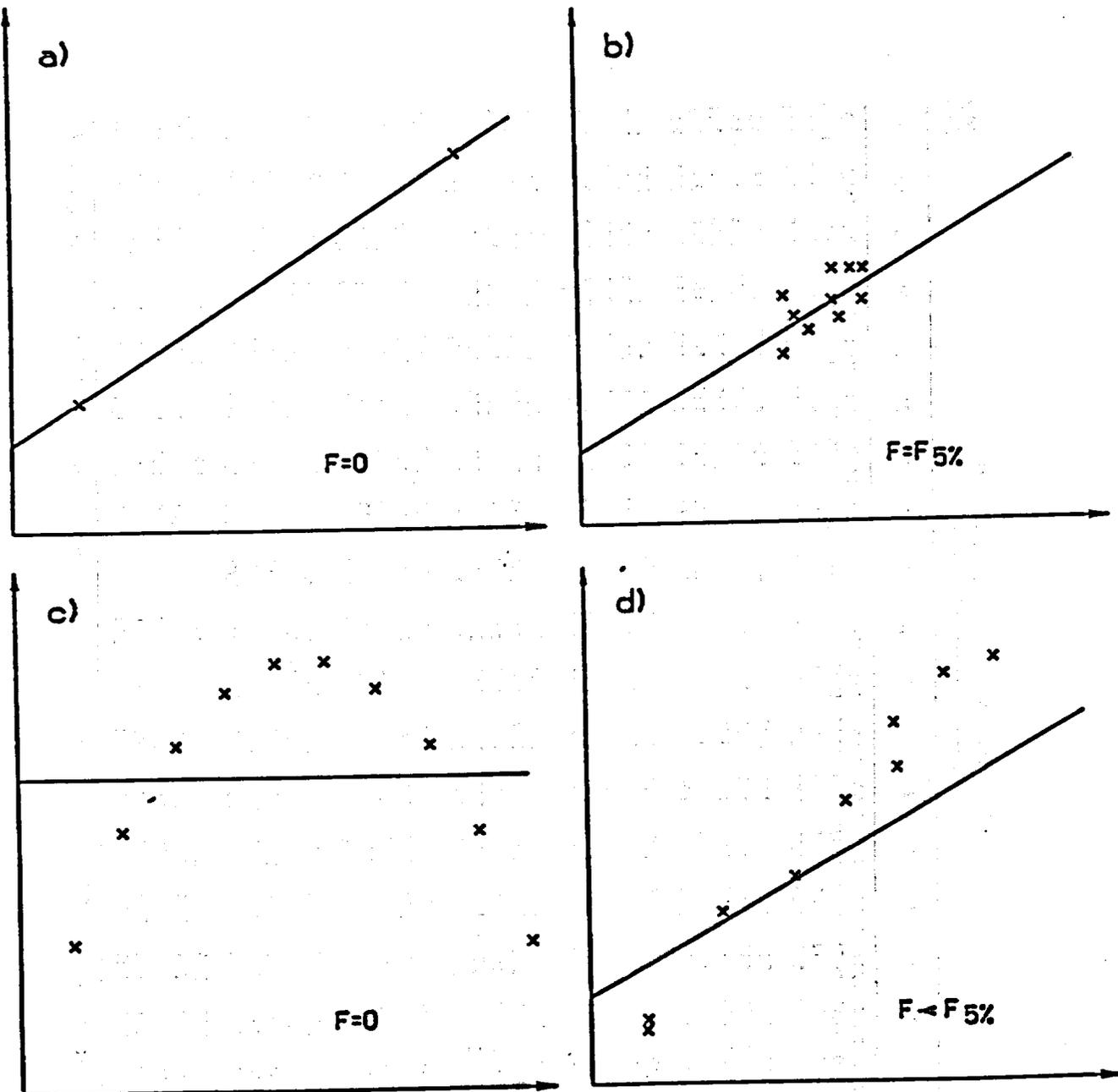


Figure 5.3 Data sets with different F-values (compared to the 95 % significance level) and correlation coefficients R.

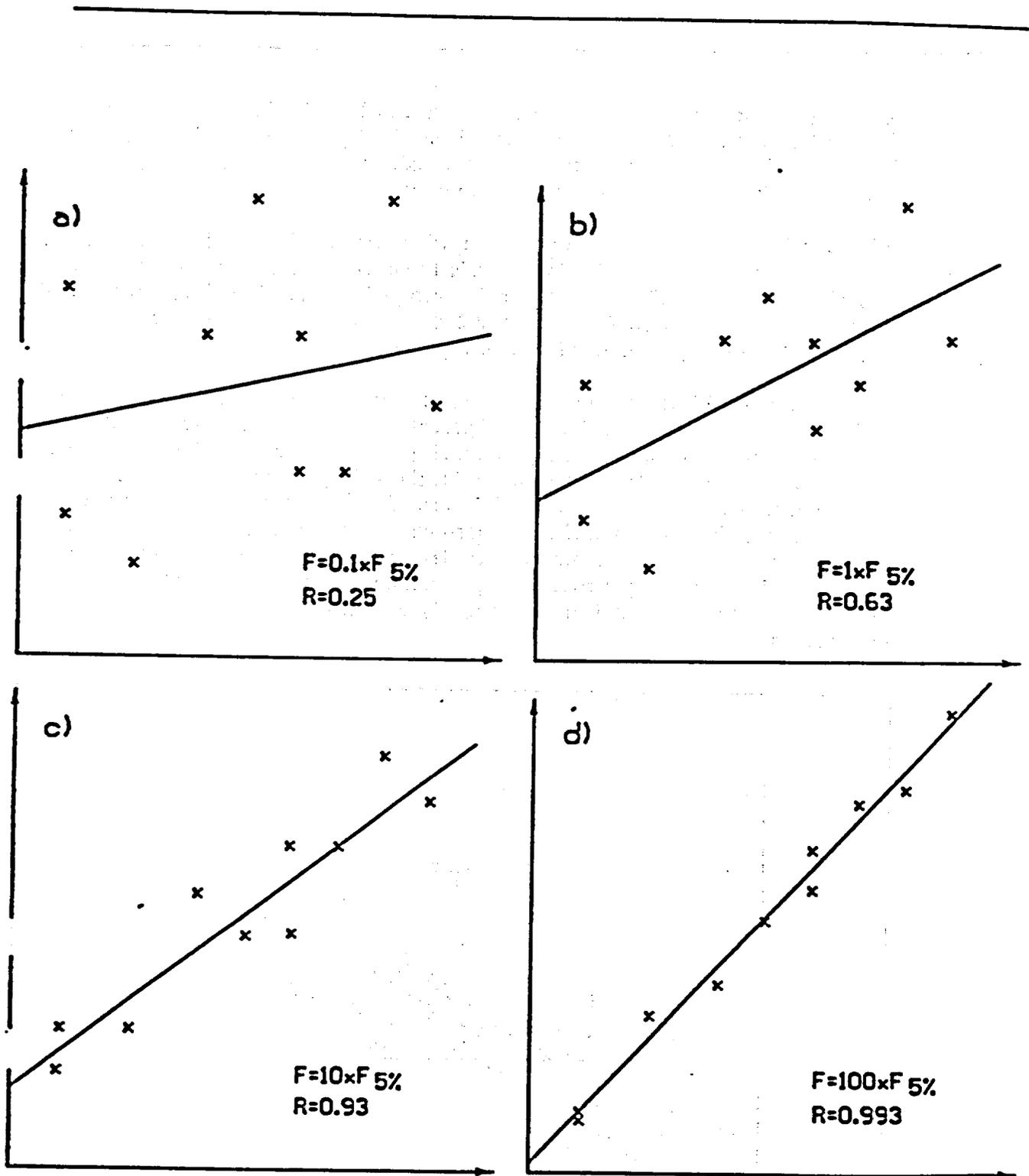


Figure 5.4 Poor examples: a) insufficient data points, b) data range too small, c) real behavior non-linear, d) incorrect entry or reference analysis.

The t-test compares the slope of the calibration curve (indep) with the slope error line (see figure 5.5). An independent strongly correlated with the dependent (analyte), will present a large t-test value, while a weakly correlated independent variable will respectively give a small t-test value. See Table F for critical t-test values.

p is the probability that the listed critical value will be exceeded in case of n degrees of freedom. For example at $(n,p) = (10,.05)$ the critical value is 2.228. This means that for 10 degrees of freedom 2.228 will be exceeded on the average 5 % of the time. Considered onwards, this means that if the t-value obtained is > 2.228 , there is a 95 % confidence that the variable being tested is strongly correlated with the dependent.

A weakly-correlated independent variable is superfluous and should not be included in the calibration, because it only introduces added precision loss (increases the error, each independent, or intensity, has a certain corresponding standard error attached to it as a result of the measurement). As a rule of thumb the t-value should be greater than 2.5 absolute (larger than 2.5 or smaller than -2.5). Note that if the real-life sample concentration range and element variation is poorly covered with calibration samples, and if there is a strong correlation between two different independent variables, both of them cannot be dropped even if both slope values are weakly correlated. In practise, this means that if two independents together give poor t-values, it does not necessarily mean that both of them are superfluous independents.

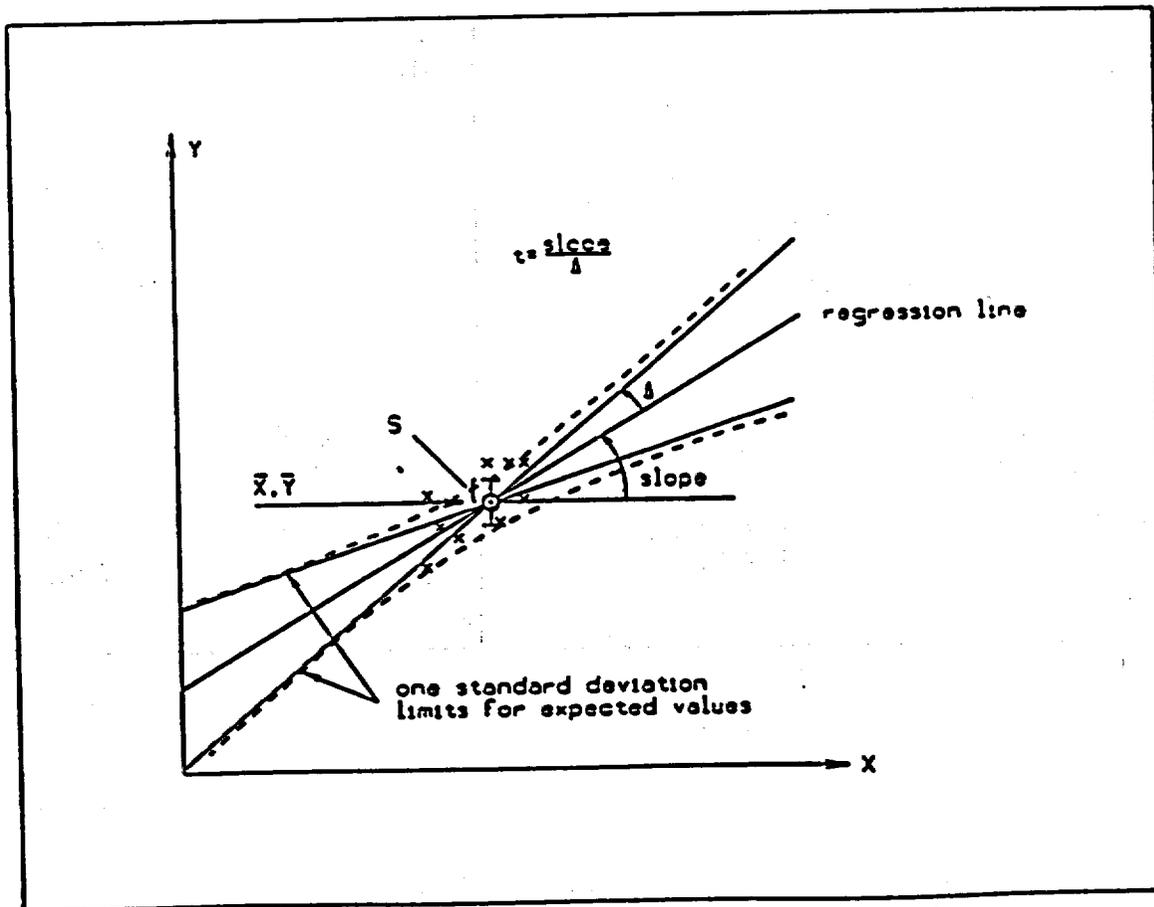
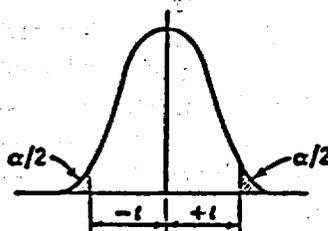


Figure 5.5 Illustration of the t-value and the confidence region of the model.

Table F Critical values of the t-test.

m = No. of independent variables

n = No. of samples - (m+1)



Distribution of t

"Probability = Area in Two Tails of Distribution Outside $\pm t$ -Value in Table"

Degrees of Freedom	Probability									
	0.9	0.7	0.5	0.3	0.2	0.1	0.05	0.02	0.01	0.001
1	0.158	0.510	1.000	1.963	3.078	6.314	12.706	31.821	63.657	636.619
2	0.142	0.445	0.816	1.386	1.886	2.920	4.303	6.965	9.925	31.598
3	0.137	0.424	0.765	1.250	1.638	2.353	3.182	4.541	5.841	12.924
4	0.134	0.414	0.741	1.190	1.533	2.132	2.776	3.747	4.604	8.610
5	0.132	0.408	0.727	1.156	1.476	2.015	2.571	3.365	4.032	6.869
6	0.131	0.404	0.718	1.134	1.440	1.943	2.447	3.143	3.707	5.959
7	0.130	0.402	0.711	1.119	1.415	1.895	2.365	2.998	3.499	5.408
8	0.130	0.399	0.706	1.108	1.397	1.860	2.306	2.896	3.355	5.041
9	0.129	0.398	0.703	1.100	1.383	1.833	2.262	2.821	3.250	4.781
10	0.129	0.397	0.700	1.093	1.372	1.812	2.228	2.764	3.169	4.587
11	0.129	0.396	0.697	1.088	1.363	1.796	2.201	2.718	3.106	4.437
12	0.128	0.395	0.695	1.083	1.356	1.782	2.179	2.681	3.055	4.318
13	0.128	0.394	0.694	1.079	1.350	1.771	2.160	2.650	3.012	4.221
14	0.128	0.393	0.692	1.076	1.345	1.761	2.145	2.624	2.977	4.140
15	0.128	0.393	0.691	1.074	1.341	1.753	2.131	2.602	2.947	4.073
16	0.128	0.392	0.690	1.071	1.337	1.746	2.120	2.583	2.921	4.015
17	0.128	0.392	0.689	1.069	1.333	1.740	2.110	2.567	2.898	3.965
18	0.127	0.392	0.688	1.067	1.330	1.734	2.101	2.552	2.878	3.922
19	0.127	0.391	0.688	1.066	1.328	1.729	2.093	2.539	2.861	3.883
20	0.127	0.391	0.687	1.064	1.325	1.725	2.086	2.528	2.845	3.850
21	0.127	0.391	0.686	1.063	1.323	1.721	2.080	2.518	2.831	3.819
22	0.127	0.390	0.686	1.061	1.321	1.717	2.074	2.508	2.819	3.792
23	0.127	0.390	0.685	1.060	1.319	1.714	2.069	2.500	2.807	3.767
24	0.127	0.390	0.685	1.059	1.318	1.711	2.064	2.492	2.797	3.745
25	0.127	0.390	0.684	1.058	1.316	1.708	2.060	2.485	2.787	3.725
26	0.127	0.390	0.684	1.058	1.315	1.706	2.056	2.479	2.779	3.707
27	0.127	0.389	0.684	1.057	1.314	1.703	2.052	2.473	2.771	3.690
28	0.127	0.389	0.683	1.056	1.313	1.701	2.048	2.467	2.763	3.674
29	0.127	0.389	0.683	1.055	1.311	1.699	2.045	2.462	2.756	3.659
30	0.127	0.389	0.683	1.055	1.310	1.697	2.042	2.457	2.750	3.646
40	0.126	0.388	0.681	1.050	1.303	1.684	2.021	2.423	2.704	3.551
60	0.126	0.387	0.679	1.046	1.296	1.671	2.000	2.390	2.660	3.460
120	0.126	0.386	0.677	1.041	1.289	1.658	1.980	2.358	2.617	3.373
∞	0.126	0.385	0.674	1.036	1.282	1.645	1.960	2.326	2.576	3.291

Abridged from Table III of Fisher and Yates *Statistical Tables for Biological, Agricultural and Medical Research* published by Oliver and Boyd, Ltd., Edinburgh, by permission of the authors and publishers.

5.3.10 Hints for optimizing a regression model

* Measure a large enough number of calibration samples that have been reliably analyzed, and cover the required concentration range of both the elements of actual interest and of the interfering elements.

* Select suitable independent variables (see sect. 2.14 and 5.3.2) by including the intensities of the analyte and the intensities of possible interfering elements in a regression model. Interfering elements often have intensities that are strongly correlated (either positively or negatively) with those of the analyte. Plotting data of e.g. $I(\text{Fe})$ vs. $I(\text{Cr})$ reveals correlations. Calibration graphs will usually reveal these correlations. Only one of any strongly related elements is necessary.

* Check F- and t-test values. Poor (i.e. low) F-test values can be improved by adding another independent variable and/or by leaving out calibration samples having relatively large residual errors. Poor (i.e. $< |2.5|$) t-test values indicate that the corresponding independent variable has only little effect in explaining the dependent. Notice that the overall standard deviation S (RMS deviation of the residuals) for a given element should not be smaller than the standard deviation obtained in a corresponding precision measurement.

Possible sources of problems

* Sample placement: keep the sample always in the same position as in calibration, rather in the center of the measurement aperture. This is especially important with pure element samples and when measuring with a surface probe

* Sample representativity: this can easily cause large deviations in results, both in particle size effects (surface), or ranges of concentrations of the elements. This factor can be expressed as the total matrix effect: the X-MET employs an empirical calibration, and corrections are based on measurements from calibration samples. Use always true samples as calibration samples, if possible.

* Reference analyses: the different methods used to analyze samples are subject to various sources of error: sample representativity, preparation errors, instrument errors, method errors etc. This can be a major source of error. Usually good correlations have been achieved with WDXRF results (powders, soils, ores, concentrates), ICP results (liquids, certain soils), AAS results (low concentrations), wet chemical results, and optical emission results (alloys). AAS and ICP results at higher (over 10 %) concentrations may introduce problems, but generally results depend greatly on the laboratory, personnel, equipment etc.

* Chemical matrix effects: these include the interferences from other elements in the samples causing secondary emission or absorption of/by the analyte's X-ray signal. Sometimes, the element causing these effects is not visible with the source employed, and a good correction cannot be made using one source only. In these cases it is worthwhile studying the performance of a two-probe model: e.g. S can absorb radiation from Cu.

* Physical matrix effects: particle size has an influence on the signal obtained from the analyte (especially in light elements), and on the backscatter of the sample

* Overlapping spectra: if neighbouring elements have a concentration ratio of 1:50...1:100, the minor element probably cannot be analyzed, especially if below ca. 0.5 %.

5.4 CALIBRATION OF AN IDENTIFICATION MODEL

5.4.1 Adding references to the identification library (ADD)

Identification models require first a pure element calibration (PUR). Install element windows for the elements in which your samples differ from each other, including major interfering (neighbouring) elements - also a channel for the BS, as usual. In PUR use at least 3 channels (2 + BS), see section 5.2.

Sample calibration of an identification model involves measuring and naming the reference samples that are desired to be included in an identification library using command ADD. These spectra will then be stored in the analyzer memory. Any future measurements that produce a similar enough spectrum of net intensities will be classified as "good match" or "possible match" identifications. The limits to these statistical identification specifications can be set with a command, THR. The capacity of the instrument is 400 references. The capacity is shared by all the identification models - you can either have them in one model or in multiple models.

Use measurement times set with TIM of 100...300 s, for AUTOSCREEN screening references 30...100 s. The measurements of the references (standards) are performed with the ADD command. This command defines the model as a "Library" model. If an ID model is existing already, the instrument displays its name and the number of references already in the library. A prompt is then given for the name of the next reference. This may include letters A-Z, space, dash (-), period, slash (/), asterisk (*), and digits 0-9. The maximum length of a reference name is 16 characters. Entering just CONT/YES gives the reference an internal name "*" followed by a number.

Next, measurement of the reference is requested. Press START from the keyboard or pull the surface probe trigger.

Example of ADD measurement (set M.TIME first):

```

> ADD
LIBRARY: CRFECU      5 REFS
6. REF: NAME?      INCO600
MEASURE           START
MEASURING: PROBE 4 TYPE SAPS
120 SECONDS LEFT...
7. REF: NAME?      END/NO
>

```

See also the note on the use of RECALC key on sect. 5.3.2.

After the library is finished, perform test measurements. Should the identification measurements present unsatisfactory results, check whether the sample used is of the same type as the ones included in the library. This includes properties such as physical form, shape, particle size, moisture content, etc. To get rid of errors of statistical origin, use longer measurement times, especially when ADDing in the references. Check also the pure elements, that they correspond with the varying elements of the samples. Ultimately, a spectrum plot can be made on the identification samples to find the sample's elemental content, and verify necessary pure elements.

NOTE: In the pure element calibration of an identification model, use a minimum number of element channels necessary, because this number effects the STDs of ID measurements.

5.4.2 Examining and renominating the reference samples (REF)

Identification library content can be viewed with the command REF. After the question mark prompt, CONT/YES and Δ are used for scrolling. '-' deletes the reference sample from the library. 'P' makes a printout of the whole library, provided an external printer/terminal is connected.

Example of an identification library printout:

```

> REF
LIBRARY 2: HI ALLOYS          17 REFS
1. REF: 304? P

LIBRARY 2: HI ALLOYS          17 REFS
1: AISI304  2: AISI309  3: AISI310          4: AISI316  5: AISI317
6: AISI321  7: AISI347  8: AISI410          9: AISI430 10: AISI440
11: F-255  12: 18-8   13: NITR 50 14: NITR 60 15: NI200
16: INCO600 17: INCO625
END/NO
>

```

Summing up, the ID calibration is as follows:

- 1) After power up or temperature change, let instrument stabilize for 30 min. in gain control position
- 2) Choose appropriate model with MDE command or MODEL key
- 3) Choose measurement time: 100...200 s for PUR, with TIM command, or M.TIME key
- 4) Change "max.count rate" to 10 kHz, if necessary, with EMP/PRM
- 5) Perform the pure element calibration with PUR command. Use at least 3 channels (2 + BS)
- 6) Let instrument do gain control for at least 5 min
- 7) Choose measurement time for ADD with TIM (or M.TIME key): 100...300 s
- 8) Measure references in with the ADD command
- 9) Should you get the message COUNT RATE TOO HIGH, use either a sample limiter, or change the max. count rate with EMP/PRM.
- 10) Document the references by getting a printout (P CONT/YES) while in REF command
- 11) Test the calibration with a short (5...30 s) measurement time, and several samples. Make several repetitive measurements from a sample. If clearly separatable (i.e. differences of several % in element concentrations) references fail to be identified, check the PUR calibration with LIM command, especially the BS sample (SPL, if necessary), which should have a similar physical form as the samples, see sect. 5.2. Check also, that the samples cover the probe aperture as well as possible. If they do not, check that there is no interfering object in the background. E.g. white tabletops contain often Ti or Ca. If necessary, use a constant background, e.g. an Al plate, especially while measuring thin samples such as foils.
- 12) Adjust the relative ranges of elements, and/or identification threshold values with THR command, see section 5.4.3.
- 13) When calibration is satisfactory, set model default time with command MTM to e.g. 5 s

5.4.3 Tuning of identification parameters (THR)

Two threshold values are used in the identification process. The identification category (GOOD, POSSIBLE, NO GOOD MATCH) is determined by comparing the TEST variable calculated from the measurement, with the coarse threshold value (UPPER) and the fine threshold value (LOWER). The THD command gives the set of LOWER and UPPER default threshold values, which are chosen automatically: e.g. with 5 pure element channels we find the 5th pair as 8.5 and 37.6 (give THD, CONT/YES and P after the first line to get a print-out).

The threshold values in use for the current identification model can be displayed and changed by the command THR. Use of ADD must precede the THR.

The thresholds may need some tuning to meet the requirements of a particular application. Higher threshold values mean broader identification tolerances with a larger accepted difference between the test sample and the reference composition. Optimum values can be found by the method of trial and error to obtain the needed separation ability. Normally for alloys the values are set to 2...3 times the default values.

NOTE! Because the threshold values depend on the number of elements present in the pure element calibration, the tuning must be performed separately for each identification model.

The adjustment of the relative ranges for different elements provides a means by which the sensitivities of the element channels can be adjusted. Due to spectral overlap it is often necessary to include elements of no particular importance into a sorting model (for example iron in steels). There are also elements, whose measurement efficiency is unusually high compared to other elements present that may be of equal or greater importance. This is due to the physical properties of the X-ray detection method. Examples of these are iron in low alloy steels (over 90 %), molybdenum in high alloy steels and tin in bronzes. Therefore it is quite useful, if the impact of these elements on the identification determination can be minimized independently.

If the relative range for an element (as a percentage of the total amount) is given as a value larger than the default value zero, the sorting sensitivity of that element is diminished. For example a relative range set to 10 % means that the sorting program allows a ± 10 % relative variation in that particular element's concentration. If the range is set to 100 % for e.g. iron in steels, its presence is essentially neglected as a sorting criterium.

The optimum relative ranges are determined by the method of trial and error starting from those elements which are present in high concentrations and have a small variation in concentration, or which have a too strong effect on the identification. Further information is available in other Outokumpu documentation especially for alloy applications. Ask at your local representative, or from Outokumpu Electronics. See references in appendix.

5.4.4 Pass/fail identification (FPI)

A pass/fail test can be done on any of the references in the model library. The instrument will compare a measurement result with a named reference. When given the command FPI, the instrument will ask for the reference name. After a reference name is given the instrument prompts to measure: each measurement result will be displayed as "PASS" (for a good match) or "FAIL" until the END/NO key is pressed.

This command can also be used for testing the identification model.

NOTE: The reference name must be entered exactly as it appears in the reference library, e.g. AISI 316 reference cannot be called as SS 316 with the FPI command.

5.4.5. AUTOSCREEN feature

The unique AUTOSCREEN feature of the X-MET 880 allows for the identification of different "families" of samples, with references in different models, be they metal alloys or different ore samples. The principle is that in a screening model, the names of the references are model names corresponding to the appropriate group of references. By changing the threshold values with THR you can set the instrument to identify a group of references as one reference, and make the instrument switch into a specific model for those references, which has a more accurate separation of the samples. A calibration scheme for alloys could be e.g. like this:

Model	Name	References
Model1	Screen ID	HI, LO, TOOL, NI, CU
Model2	Screen Assay	HI, LO, TOOL, NI, CU
Model3	HI	AISI 304, 316, 321 etc. Stainless steels ID model
Model4	HI	AISI 304, 316, 321 etc. Stainless steels assay model
Model5	LO	AISI 4140, 4370, 4740 etc. Low alloy steels ID model
Model6	LO	AISI 4140, 4370, 4740 etc. Low alloy steels assay model
Model7	TOOL	TS-2, TS-6, etc. Tool steels ID model
Model8	TOOL	TS-2, TS-6, etc. Tool steels assay model
Model9	NI	INCO 600, INCO 700 etc. Nickel alloys ID model
Model10	NI	INCO 600, INCO 700 etc. Nickel alloys assay model
Model11	CU	CDA188, CDA451, CDA716 etc. Cu alloys ID model
Model12	CU	CDA188, CDA451, CDA716 etc. Cu alloys assay model

In this way, a library of models can be built. The library can contain also another screen model. The references in the screen model (model 1) represent the extremes of the group of references: lowest alloyed and highest alloyed, also in-betweens, if the group concentrations differ in several elements, as stainless steels (Fe, Ni, Cr, Mo, Co). You must give several references the same name in order to "guide" the X-MET to the right model. E.g. in the above case, references in model 1 with name HI could be AISI 303, AISI 321, AISI 310, AISI 317, AISI 347 and CARPENTER 20.

As a general rule, low alloys should be measured "in" with a longer (100...200 s) time, and high alloys with a short (30 s) time into the screen model. As to the actual ID models, normal rules apply. Also, the THR values of the screen model (1) must be changed: e.g. to values 5000 for FINE, and to 50 000 for COARSE thresholds.

NOTE: The instrument changes the model automatically, and returns to the screen model, when a new measurement is started. Should you want to select a specific model, press the MODEL key, new model number, CONT/YES, and finally END/NO. This causes the X-MET to end autoswitching, and remain in the target model.

5.5 POST-CALIBRATION ADJUSTMENT PROCEDURES

5.5.1 Manual normalization (NOR)

In course of time, the decay of the radiation source reduces the acquired intensities. This can have dramatic effects on the results of quantitative analysis, if not properly compensated for. The NOR command provides a means for this. NOR must be carried out regularly by the user. Normalization increases the value of the normalization coefficient, which is used as a multiplier of the counted pulses in a pure element window.

Model normalization will be necessary after a source-dependent time interval has elapsed from the calibration.

A manual normalization is needed to compensate for the decay of the radioactive source. The time interval for a 2 % decrease in the source activity is as follows:

Recommended NOR interval

Fe-55	29 days	1 month
Cm-244	190 days	6 months
Cd-109	13 days	2 weeks
Am-241	12.6 years	1 year

Carry out a normalization with one of the pure element samples in the model. Select an element from the middle of the source's element range (see element ranges at end of Ch. 2), preferably one, which gives less than 6000 c/s, and which does not need a limiter ring. If a limiter ring (or slot) has been used in the pure element calibration (PUR) with the normalizing element, the same limiter (geometry) has also to be used with the NOR command. Use a 200 s measurement time, and make sure the normalizing sample is centered over the aperture. For this purpose, use the supplied pure element centralizing ring with HEPS and LEPS probes, or supplied calibration stand with SAPS and SLPS.

Good normalizing samples are e.g. Si, Cl or S with the Fe-55 source, Cr, Mn and Co with Cm-244 and Cd-109 sources, and Cu, Zn or Pb with the Am-241 source. Always check the sensibility of the normalization coefficient: it should be 2.000 after a period of one half-life of the source from the calibration.

NOTE: The BS sample cannot be used for normalization. All the assay models associated with a probe have to be normalized separately. ID models need not be normalized.

Example:

```
"M.TIME"
NEW MEAS. TIME (SECONDS)? 200
> NOR
NORMALIZING SAMPLE? FE2 (probe n:o 2)
MEASURE START
MEASURING: PROBE 2 TYPE HEPS
200 SECONDS LEFT
```

```
NORMALIZING FACTOR : 1.187
>
```

Several probe models and distributor boxes

When normalizing a model for several probes, each probe is simply normalized separately, by giving command NOR, and the normalizing pure element sample along with the number of the probe, e.g. Fe2.

DOPS normalization

DOPS normalization is carried out similarly: the difference comes in telling the instrument which source is to be normalized: give NOR, and e.g. Fe6A for the A source (higher source energy) and probe number 6, or similarly Cr6B for probe 6 and B source. If the model has measurements with both sources, then the model also should be normalized with both sources.

NOTE ! Identification models need not be normalized.

Normalization coefficients

The normalization coefficients can be examined (LIM), and changed (EMP/PRM) manually. Select a model (MODEL key) and read the values of the normalization factors with command LIM. The latest normalization factor values are displayed, along with window limits. Right after the pure element calibration, the normalization constants are 1.000. After a time corresponding to the source half-life, the coefficient should be 2.000, if the same calibration has been employed since, and normalization procedures performed on schedule. For manually changing the normalization constants, use command EMP/PRM - Channel parameters. Read-out example: Channel 1. Ti

```

> EMP
> PRM
GENERAL PARAMETERS? END/NO
CHANNEL PARAMETERS? CONT/YES
CHANNEL: 1 ? CONT/YES
ELEMENT: TI ? CONT/YES
PROBE NUMBER: 1 ? CONT/YES
SOURCE: A ? CONT/YES
CHANNEL LOW LIMIT: 53 ? CONT/YES
CHANNEL HIGH LIMIT: 62 ? CONT/YES
PEAK CHANNEL: 58 ? CONT/YES
NORM. COEFFICIENT: 1.34979 ? CONT/YES (or enter new value)
NORM. INTENSITIES: 656.21996 ? CONT/YES
CHANNEL: 2 ? END/NO

G MATRIX ? END/NO
ASSAY/IDENT PARAMETERS ? END/NO
>

```

NOTE! The CONT/YES confirmation associated with commands such as EMP or PRM is not shown here. However, all command strings are executed only after the CONT/YES key is pressed. This is similar to the use of the Enter/Return key in computers and data terminals.

Notice the use of END/NO-key after the normalization intensity value for channel 1 has been displayed: in fact, one could give END/NO right after the NORM.COEFFICIENT also. In this case it finishes the enquiry of channel 1 parameters and proceeds to channel 2 parameters. Further END/NO pressing leads to the next subroutine under PRM command (G MATRIX). One can also have the whole set of model data sent to a (printer) terminal by giving P command:

```
> EMP
> PRM
MODEL 6 ?
GENERAL PARAMETERS ? P CONT/YES
```

This produces an output of all the model parameters for model 6 on a printer/terminal.

5.5.2 Standard sample measurement and corrections (MST, STA)

After normalization is performed, the last fine tuning of an assay model should be made with a standard sample correction. An assay model can be adjusted with the aid of a standard sample. A standard sample is initially installed with the command MST, right after the calibration. A standard is given a name, measured, and the resulting concentrations are stored into the memory as a future reference. A good standard sample is e.g. a calibration sample with a small standard residual (see under command MOD-residuals), the concentrations of which are in the mid-range. The assay values reported and memorized can be changed with the same command: give END/NO to the prompt MEASUREMENT?, and you can change the values. They should be close to the model approximations for that sample, i.e. the estimates. If not, check all model parameters and make a new measurement, if necessary. NOTE: Use similar measurement times as in CAL, e.g. 200 s, for the MST. Do not change the memorized (measured) standard assay values to the reference assay values, if not close to the measured values. Note, that liquid samples can have crystallizing components, or that they can evaporate from even a closed sample cup, so that they should be stored in an appropriate container.

Example of MST:

```
> MST
STANDARD NAME: STD73
MEASUREMENT? CONT/YES
MEASURING: PROBE 1 TYPE SAPS
200 SECONDS LEFT...

ASSAYS: FE 18.81 CU 1.273 ZN 5.147
>
```

After a standard is created with MST, the periodic standardizing measurements of the same sample are to be made with command STA, after normalization. The new, measured, concentration results are compared to the ones stored, and the model parameters (intercepts) are adjusted, if necessary. After the execution of STA, the relative deviations of each element concerned are displayed. Should the absolute value of a relative deviation exceed 3, model parameters (intercept values) are adjusted automatically with respect to that particular element. If the measured concentrations differ severely (by over 20 standard deviations, STD's) from the ones stored in MST, error message WRONG STANDARD is displayed and no corrections are made. In that case, check the standard, and make a new measurement with

STA. Make sure, that the instrument has been stabilized for 30 min. before making a STA measurement. Check also, that the normalization values are sensible. If the problem cannot be resolved by normalization or remeasurement, it will be necessary to reduce the STA time with EMP/PRM, and then remeasure with STA. Start with 10 s, then 60 s before returning to 200 s standardization.

In a model using several probes, a measurement on each probe is requested before correction calculations are made.

6. MEASUREMENT

6.1 Performing a measurement

In order to accomplish reliable measurements, the analyzer has to be properly calibrated for the application in question. Refer to Chapter 5 on calibration issues.

After the proper preparations have been carried out and the instrument has been allowed a stabilization time, proceed according to Sects. 6.2.1 or 6.2.2, depending on the probe type used.

WARNING ! Do not use or calibrate the instrument closer than 1 m to a monitor screen, TV set, CRT or any other strong source of electromagnetic radiation.

6.2 Using the different probes

6.2.1 The HEPS and LEPS probes

Open the probe lid. Check that the sample cup used is undamaged and clean, that the plastic films are intact and clean (both in cup and cup holder), and that no particles can enter the probe. Place the sample in the sample cup. The instructions for the handling of the calibration samples apply equally to actual samples, especially concerning penetration depth values (sect. 4.6), and amount of sample. Press a powder sample with the supplied piston tool (brass). Wipe the cup against soft paper or a cloth to remove adhered dirt, or to detect possible leaks in a sample cup.

Close the probe lid and slide the measurement base backwards all the way to the extreme position. The probe is now ready for a measurement.

Press **START** to begin a measurement. The first second is used for evaluation of the detected count rate. If it is within permissible limits, the actual measurement is performed. Should you

get an error message, unsatisfactory results, or the measurement will not start, refer to Chapter 9.

If a sample gives a message: **COUNT RATE TOO HIGH**, your samples either differ in concentration noticeably from the calibration samples, you have no limiter, or the **MAX.COUNT RATE** is set at a too low value, see **TCR** and **EMP/PRM** commands.

NOTE: Limiters cannot be used unless they have been used in calibration also.

Figure 6.1 illustrates the effect of a limiter ring on the intensity of fluorescence radiation when radiation that does not penetrate the material of the limiter ring is detected. This also forms an indication to the size of the aperture required to reduce the count rate by a certain percentage.

Properly chosen limiters do not have effect on the spectrum peak locations. If the limiters are, however, used to decrease the count rate in connection with sample calibration, all the calibration samples must be measured with the same limiter.

If the excessive count rates occur repeatedly, the radiation intensity of the source should be reduced by placing an absorbing filter in front of it. This requires a special licence to handle radioactive sources. A serious risk of radiation occurs. See sect. 8.5.

NOTE: When using limiters, you also effect the standard deviation of the measurement. Accordingly, you should use longer measurement times to compensate for the decrease in intensities.

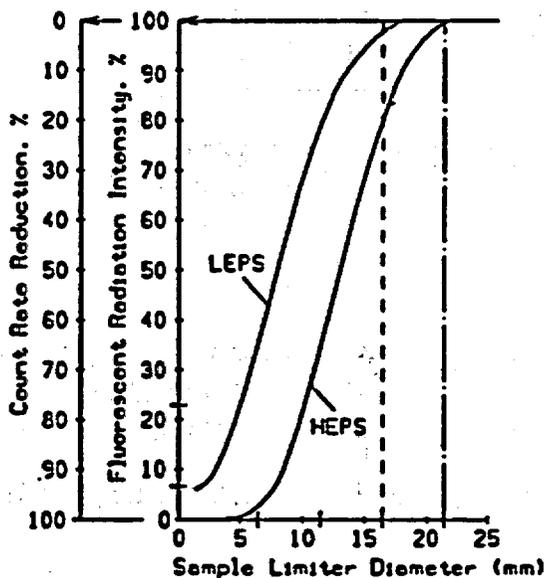


Figure 6.1 The effect of a limiter ring.

6.2.2 The SAPS, DOPS and SLPS probes

The actual measurement is done through the small measuring window in the bottom of the probe. Hold the probe against the surface of the sample to be measured. Watch out, though, not to damage the measurement window as it is of plastic film, especially in the SLPS probe. The SAPS and DOPS probes must not be pressed too hard, as not to damage the shutter mechanism.

Pull the trigger (or press START) to begin a measurement. The LED indicator of a SAPS or DOPS is lit, and the one on an SLPS turns green. If the shutter doesn't stay sufficiently open, the indicator goes off (or turns red in SLPS) and the measurement is interrupted. In this case start the measurement again. Otherwise, similar information applies as with HEPS and LEPS probes.

6.3 Single key commands associated with measurements

The START key

The START key starts the measurement with a HEPS, LEPS or SLPS probe. The remaining measurement time will be visible on the display. END/NO key can be used to interrupt the measurement. At the end of measurement, an audible signal is given and the concentrations or the identification result is displayed.

Examples:

```
ASSAYS: FE 53.4 CR 29.3 CU 10.8
>      PB 0.345 ZN 5.51
```

```
-----
NEAREST REF:      INCO 600
>                GOOD MATCH 5.321
```

The MODEL key

The MODEL key is used to change the current model. When this key is pressed, X-MET prompts for the number of the new model (1 to 32). CONT/YES and END/NO retain the default model. The current model number is displayed in the lower right-hand corner of the display.

With "autoscreen" calibration, press END/NO after you select a new model and want to stay there.

The M.TIME key

The MTIME key is used to change the measurement time. The measurement times are expressed in seconds, the possible values being between 1 and 32767. CONT/YES and END/NO retain the default measurement time. The current measurement time is displayed in the upper right-hand corner of the display. Model default time is changed with the command MTM.

The RECALC key

Results from the latest measurement can be recalculated again in any model. This is done by switching to a new model, and pressing the RECALC key. If the new model is for several probes, a new measurement has to be carried out, i.e. recalculation is not possible. If the model with which the original measurement was made was for several probes/sources, then only the last measurement can be recalculated. Note also, that the probe number is not checked for in the new model.

The function keys F1 - F5

The five function keys can be programmed to contain a command expression. The programmed expressions are stored in the analyzer's memory. The programming is done with the command FNC. The commands under the function keys are executable even when the keyboard is locked (LOC).

6.4 Other commands

In this section commands associated with the everyday use of the analyzer are discussed. Commands associated with the calibration procedures are found in Chapter 5. For a list and description of maintenance mode commands, see sect. 8.7.

AMS : Average of several measurements

AMS calculates cumulative average values for a series of measurements. Once started, the command will prompt for a new measurement, which is initiated with the START key. The series is finished with END/NO, after which the corresponding mean values are computed and displayed.

BLT : Backlight on/off

This command toggles the display backlight on and off.

CAO : Configuration of the analog output

With CAO the analog output is set to follow the concentration of a particular element during a subsequent CMS. This produces a graph on an external X-Y-plotter. After CAO is started, the user is prompted for the model and the element to be followed. The SCALE? prompt is replied with the element concentrations that are to be set to the full scale output voltage values (0-5 V). The given range follows the concentration linearly. Both the average or the latest measurement value can be plotted. Note, that only one element can be followed at a time.

The use of the analog output is terminated after the CAO MODEL? prompt is replied with a 0.

CHR : Send characters to serial interface

A set of any standard ASCII characters can be sent to the serial interface using the command CHR. The characters are expressed as decimal ASCII codes and separated with spaces. The input is terminated with END/NO.

Example of CHR. "0[CR][LF]" is sent.

```
> CHR
ASCII CHARACTER CODES (DECIMAL):
48 13 10 END/NO
```

CMS : Continuous measurement

In order to operate, the model sequence must be set first by the command SEQ. Here you set the number of the model(s) you want to make the measurement in.

The command CMS starts a continuous measurement cycle. The measurement interval is determined by the model default measurement time (set with MTM). The cycle will go on until terminated with END/NO, or when interrupted. The instrument will continuously report the latest measurement result.

The format of the results can be chosen as assays (concentrations) or gross count rates in each element channel. The output can also be given a header text. After each measurement period the current time and results of the last measurement cycle are displayed for each element concerned.

Command CMG is only for on-line measurements, and should not be used otherwise. A separate manual is available for on-line installations.

The use of the CMS command requires a terminal (printer or computer).

Example of a CMS printout:

```
> SEQ
POSITION 1: 0? 3 (You wish to measure in model 3)
POSITION 2: 0? END/NO
>
```

```
> CMS
ASSAYS ? CONT/YES
HEADER ? CONT/YES
SAMPLE 1013 CONT/YES
END/NO
```

```
***** X-MET 880 Continuous measurement: Concentrations*****
Date: 13.09.91
```

TIME	MODEL	CR	FE	NI	CU
15-49-21	STEEL	14.75	77.08	2.998	3.354
15-53-40	STEEL	14.69	77.30	2.895	3.324
...	etc.				

NOTE: The CMS command cannot be used with SAPS or DOPS probes.

CSI : Configuration of the serial interface

This enables the operator to select an alternative communication speed for the X-MET serial port. The possible values are 50, 75, 110, 134.5, 150, 200, 300, 600, 1200, 1800, 2400, 4800, 9600 and 19200 bauds.

The CONT/YES or Δ keys are used to scan the values. Use END/NO to select the new baud rate.

The printer, terminal etc. connected to the serial port must use the same communication speed.

DEL : Delete model

The DEL command deletes a model. The storage space can be used for a new model, and all parameter values, including time, are set to default values. Therefore deleting a model with the DEL command means that a new pure element calibration and a new sample calibration will be required. Also, the measurement time is set to 15 s, and the max. count rate to 6 kHz.

Example of deleting model 6

```
> DEL
WHICH MODEL TO DELETE (1-32)? 6
DELETE MODEL 6: CRFECU? CONT/YES
DELETED
>
```

DTM : Display time

Displays the system time and date. Press END/NO to terminate.

HLP : Help command

This command gives, when used with a terminal, a list of all the commands used by the X-MET 880, and a short description for each one. If an EMP/HLP is given, then service commands are also printed.

INT : Intensity output

Computes and displays the intensities (= net count rates) of the element channels in the current model, as accumulated in the latest measurement. CONT/YES and Δ scroll forward and backward, P CONT/YES after any line sends output to a printer in a table form.

LOC : Lock the keyboard

Locks the X-MET keyboard into a state in which it will accept only the START, MODEL, M.TIME, RECALC or CTRS +/- keys, the function keys F1 - F5, and the command UNL. The locked state is preserved even if power is switched off or the battery pack is changed. This allows the use of the instrument without concern of someone changing the calibrations.

UNL : Unlock the keyboard

Releases the keyboard lock set with LOC.

MDE : Change model = <Ctrl>-D

This command is the same as MODEL key. After the command responds MODEL X?, a P, CONT/YES will produce a list of the models on a printer.

MTM : Set model default measurement time

With this command you can change the default time of each model.

PUL : Pulse frequency output

Reads and displays the gross count rates in the current model element channels, as accumulated in the latest measurement. CONT/YES and Δ scroll forward and backward, P CONT/YES sends output to a terminal after any line.

REC : Recalculation = <Ctrl>-R

This operates the same as the RECALC key.

STD : Standard deviations

STD computes the statistical standard deviations of the concentrations based on the latest measured spectrum.

The display format is similar to the one of the concentration output:

> STD

STDEVS: FE 0.040 CR 0.361 CU 0.142 PB 0.006

Take into account that this does not reflect the total error of the measurement but only the part due to counting statistics. In general it is a good summary of the instrument's precision (repeatability). The results on the same sample should stay within $\pm 3 \times$ STD value. The statistical part of the error can be reduced by using a longer measurement time. Note, that the STD value should always be smaller than the RMS error (S) of the model for any element.

STM : Set time

Allows the user to set the system time and date. If the battery is disconnected or discharged, the system clock will be reset to its initial value.

The date is entered as day.month.year, the time is set as hours-minutes-seconds. If the seconds part is omitted, it will be assumed as zero. The prompt PRINT? allows the user to choose a date-time printing in the beginning of every measurement, by responding CONT/YES. An END/NO answer will not produce this data.

STR : Start measurement = <Ctrl>-A

This operates the same as the START key, or the trigger on SAPS or DOPS.

TCR : Total count rate

Displays the total count rate (counts per second over the whole spectrum) for the latest measu-

rement. Use this to check the count rate of the most "concentrated" calibration sample, in order to see if the samples need a limiter, or to determine if the MAX. COUNT RATE needs to be changed.

Total count rate from a sample should be in the range of 1500...6000 preferably, minimum value being ca. 800...900. Also, the count rate from the reference should be above the minimum value. If below this, either a filter needs to be taken off from the source, or the source needs to be replaced. NOTE: In e.g. alloy applications, count rates over 6000 are common.

TIM : Change measurement time = <Ctrl>-T

With this command you temporarily change the measurement time. Also, with this command you set the measurement time for the pure element calibration, PUR. The same as the M.TIME key.

7. OPTIONAL EQUIPMENT

7.1 External terminals

The X-MET 880 analyzer can be used through an external terminal (printer or computer). The X-MET serial interface supports most commercial data terminal types, as long as they can be configured as described in sect. 3.8.2. The X-MET communicates in standard ASCII code.

Use of an external terminal provides the user with a larger screen and an improved keyboard. The special keys of the X-MET keypad can be accessed as follows from the terminal keyboard:

CONT/YES	Enter
END/NO	Esc
START	STR or Ctrl-A
MODEL	MDE or Ctrl-D
RECALC	REC or Ctrl-R
M.TIME	TIM or Ctrl-T

Command *** (comment) produces output to terminal without X-MET response. For the link between the external computer terminal and the X-MET 880, a communications cable is necessary. Sometimes it may be necessary to acquire also a gender changer and/or an adaptor connector for the printer cable (standard accessory). See sect. 3.8.2.

A PC or equivalent needs a terminal emulator program, e.g. PROCOMM®, KERMIT®, CROSSTALK®, SYMPHONY®, WORKS® etc. to be able to communicate with the X-MET.

7.2 Printers

External printers can also be used through the serial port. X-MET can communicate with most commercial matrix, daisy wheel, inkjet and laser printers, provided the communications configurations described in sect. 3.8.2 are met. See the Owner's manual of the printer for communication parameters settings in the printer. It must have a serial port, and at least 1 KB

of buffer memory.

Several commands produce output in table form for printouts. These are executed most often with P CONT/YES. Command SPL is used to print measured spectra in a graphical (histogram) form (see sect. 5.2.6 for the use of SPL).

For the link between the external printer and the X-MET 880, a communications cable is necessary (standard accessory).

7.3 Data loggers

A special software package GRABBER is available for the handheld PSION Organizer[®] data logger. This makes on-site event recording possible, with up to 200 measurement results stored in the data logger. Also, the PSION data logger acts as a terminal, through which the instrument can be manipulated, if e.g. in a backpack. The data from the logger can easily be loaded on a computer disc in a file form. The GRABBER accepts only assay form data, not ID results. Contact a representative of Outokumpu Instruments for further details.

7.4 Personal computers

When equipped with the appropriate emulation software, most personal computers can be used in place of the data terminal of sect. 7.1.

There is, however, also a proprietary software package, ESP, available. It provides many features that can not be accessed from a plain terminal or an emulator program. This package is an Outokumpu Instruments X-MET accessory, and runs under PROCOMM +[®] in MS-DOS[®] computers. Ask for more information from your local representative, or from Outokumpu Instruments.

8. MAINTENANCE

8.1 Introduction

The following chapter is provided to support the X-MET operating instruction manual. It covers routine maintenance operations, and when exploited fully, saves valuable time and money for the user's benefit. The covered themes include radiation safety matters, normal maintenance procedures and source handling. It must be pointed out, however, that in case of an actual malfunction the user is to contact a representative of Outokumpu Instruments immediately for further information. **THE PROBES ARE MADE UNSAFE IF COVERS ARE REMOVED BY UNSKILLED, UNQUALIFIED OR UNLICENCED PERSONS.** In most countries a special licence is required to work with radioactive material. Also, a licence from Outokumpu Instruments is required.

8.2 General probe maintenance safety considerations

The X-MET probes contain a nuclear radiation source. For this reason special care should be taken if disassembling a probe. Considerations should be made before opening the probe, with

regards to the source and its shielding, together with the task you plan to carry out.

Most countries have strict legislation and special regulations concerning the use and handling of radiation sources. These regulations must be followed.

IN GENERAL, SOURCE HANDLING SHOULD ONLY BE PERFORMED BY A REPRESENTATIVE OF Outokumpu Instruments. If it is necessary to dismount the probe for source replacement etc., the following steps must be strictly followed:

1. All tools required for the job are not only available but at hand. Phillips and PZ screwdrivers of two sizes will be needed.
2. A suitable lead container or cover for shielding the source is available. Supplied as an accessory.
3. In SLPS, HEPS and LEPS probes, the source is visible after the midpart and the top are separated. First unscrew the bottom (or top in SLPS) part, then unscrew the midpart screws inside. Be careful for the microswitch connector cable. In SAPS and DOPS, the source is behind the shutter. Open the screws on the side of the probe. In SAPS the source holder is pressed between two pins. The source is to be covered with the appropriate lead shield as soon as possible.

When detaching the source holder, be careful not to scrape the surface of the source or the detector window. Both are extremely thin!

4. The source is to be handled with tweezers, pliers etc. **DO NOT TOUCH THE SOURCE WITH BARE HANDS.**
5. When properly covered with a lead shield or when inside a proper source container, the source presents no radiation hazard. **THE SOURCE MUST NOT BE LEFT UNCOVERED OR UNATTENDED.**

Storing the source in its holder is recommended.

6. When installing a new source in its place, make sure that the source is securely fastened. Even small variations in source position affect the measurement geometry (results) drastically. Make sure, that all relevant parts (filter(s), source, washers, Seeger ring etc.) are in place and in correct order (sample > (filters, Al on top) > source > (filter) > spring washer > seeger ring > detector), and that the active surface of the source is to the correct side (upwards). See figure 3.9.

For a DOPS probe, the B-source or the source with the lower energy is to be located on the trigger side, that is when the trigger is released, the source is in front of the detector window.

7. The active side of the source must not be pointed at a person or anything that might be damaged by radiation. Notice, that the X-ray photons emitted from higher energy sources penetrate easily most non-metallic materials, e.g. a table top. The radiation emitted from the bottom of the source is practically zero.

8.3 Preventative maintenance

In order to ensure the highest measurement accuracy, the probe condition must be checked regularly. The resolution of the probe (detector) should not exceed 18% calculated at the Mn K_α energy of 5.9 keV (refer to TSM; sect. 8.7). Also depletion of the radiation source activity has a significant effect on the measurement accuracy. This applies especially to Cd-109 source due to its relatively short half-life.

The probe electronic and the detector are sensitive to air moisture. To prevent any adverse effects, a silica-gel bag is contained in the probe electronic unit. This has the ability to absorb excess moisture. The remaining efficiency of the silica-gel can be determined by its color.

Blue	100% efficient
Clear	50% efficient
Pink	Inefficient

If the silica-gel has turned pink, the bag must be replaced, or regenerated by placing it in a hot oven (105-130°C) for 2...7 hours.

In outdoor use, the silica-gel bag should be renewed at least once a year (DOPS & SAPS probes); neglecting this will result in a shortened detector lifetime. Working continuously in humid environments (above 65 % rel.humidity) requires replacement of the silica-gel even more often. Ask your local X-MET representative for more information.

8.4 Cleaning the probe

When sample cups are being used, it is very important to make sure that there is no damage done to the film on the base of the sample cup, or the cupholder film; similarly, the window of a surface type probe must be intact. When using sample probes avoid dropping powders or liquids on the probe: attempting to blow powders away may force them in the probe instead.

If sample or dirt should enter the probe, the probe will have to be cleaned without delay to avoid impairing the measurement capability of the detector, and the inevitable risk of damaging the beryllium detector window. Dismantle the probe taking into account the guidelines given in sect. 8.2. Having removed the cover plate and the source holder, place the source with the holder in a lead container provided for the purpose. The removal of any loose dirt should be done with a soft brush or cloth and then blown with air. To remove adhering dirt a solvent may be used.

The beryllium window of the detector is extremely thin. Should it be necessary to clean the beryllium window, extreme care must be exercised to prevent any permanent damage. The window of the detector can be cleaned with pure ethanol (99 %) or acetone and a cotton swab. **DO NOT** use water (or diluted ethanol) on the detector window as corrosion will occur which will in time destroy the detector. Avoid touching the beryllium window as the oxide produced is toxic and the window is easily punctured.

8.5 Reducing the radiation intensity

For reliable measurements a suitable radiation intensity must be obtained from the source. Too high a rate of detected pulses is equally unfavorable as a too low one. The radiation intensity

depends on the measured sample concentrations as well as on the activity of the radiation source.

Optimal total count rate (TCR; sect. 6.3) for a measurement is between 1500 and 5000. Should it exceed 6000, X-MET prompts COUNT RATE TOO HIGH. If the excess is not of considerable extent, the measurement can be continued (CONT/YES). At this point, however, the measurement conditions are not optimal, and the best accuracy cannot be reached. Also, it usually is an indication that the sample being measured differs in concentration from the calibration samples.

Should it be necessary to reduce the radiation intensity emitted from the source, various combinations of pure aluminum or iron filters (absorbers) are placed between the active surface of the radiation source and the sample. The activity of the source diminishes over a period of time and therefore makes it necessary to remove some of the absorber foils to re-establish the required intensities. (Note: this applies to Cd-109 in particular). The half-life periods associated with the X-MET sources are listed in Table G.

Table G Source half-lives.

Source	Half-life
Fe-55	2.69 years
Cm-244	17.8 years
Cd-109	462 days
Am-241	433 years

Table H lists the effects of plastic (mylar), aluminum and iron filters (absorbers) on radiation from different sources.

Table H Transmission ratios of filter-source combinations (absorbers).

Source	Transmission %		
	0.2 mm Mylar	0.25 mm Al	0.05 mm Fe
Fe-55	70 %	0.02 %	0 %
Cm-244	95 %	50 %	6 %
Cd-109	97 %	85 %	45 %
Am-241	ca. 100 %	ca. 100 %	95 %

Filters can be added or removed by dismantling the probe and following the source handling guidelines given in sect. 8.2. Remove the source holder from its place. Next, remove the source from the source holder and store it in a lead container provided for the purpose. Install a filter (or several, as required) in the source holder. Use Table H for estimating the amount and

quality of the absorbers required. Finally, insert the source in its place. **NOTE:** For high energy sources (Am, Cd) it is advisable to use an Al filter always on top, if using an Fe filter, in order to stop the Fe radiation. With the Cm source, a Fe filter should not be used at all.

Assemble the probe. Carry out a measurement using one of the samples from the series to be studied. Use TCR command to check the total count rate of the reference, and a sample.

NOTE! When using filters to reduce the intensity of a radiation source, additional care must be taken so that the reference sample can still be measured reliably. This is done by inspecting the reference spectrum quality, resolution and TCR, all of which must remain within the acceptable limits (TCR > 1 500). Otherwise the effectiveness of the gain control procedure will be reduced severely.

8.6 High voltage adjustment (spectrum positioning)

The probe is tuned for the particular source by adjusting the gas amplification of the proportional counter. This is done by adjusting the detector voltage, which can have values from 500 to 1000 V. Changing the detector HV (high voltage) moves the measured spectra along the X-MET microchannel range. The setting is correct when the backscatter peak is in its place at the end of the channel scale (255), and the measured pure element sample is located as seen in Table I.

Table I Probe tuning.

Probe(s)	Sources	Sample used	Peak channel
LEPS or	Fe-55	Si	73-77
SLPS	--"	--"	--"
HEPS or	Cm-244	Fe	98-102
SAPS or	Cd-109	Fe	76-80
DOPS	Am-241	Zn	71-75

Due to its unique double-source nature, tuning the DOPS probe demands a few extra remarks. DOPS can be tuned on either of the sources (though using only normal procedures, A-source or the source with the higher energy is much more convenient for this). The dynamics of the tuning procedure can then be checked on the other source. The table values above apply for DOPS sources as well, with the exception of the Fe-55 B-source, which should be tuned on Ti for channels 93-97. Should you yet find unsatisfactory results, check the order and type of the sources. **NOTE!** In DOPS, the gain for A-source is twice that of the B-source. Therefore the B-source backscatter peak will be found in the measurement range (approx. ch. 130-140). This is normal.

The actual adjustment procedure is done with the DIP switches located on the probe XHVU board. In all probes, the switches are visible after removing the probe cover.

Additional care should be taken, so that live circuits are not short-circuited when adjusting the HV. This applies especially for the detector-end components.

Before any adjustments are made, a note should be made of the original settings. The switches form a 8-digit binary number, bit 8 being the least significant bit (LSB), and bit 1 the most significant bit. Switching bit n:o 8 on (or off) moves the spectrum 0,5-2 microchannels, depending on the associated probe electronics.

During the adjustment the probe must not be allowed to perform gain control: either the probe is uninitialized, or the probe is not allowed to remain in the gain control position (sect. 5.1.3).

Carry out a few test measurements (TSM) on different voltage values to set the pure element spectrum peak on the desired value. If the spectrum can not be found, a good procedure is to start either from a mid-way setting (that is: 1000 0000), or from the backscattering spectrum. This is started from the smallest HV value (being 0000 0000), and continued upwards until the backscatter peak appears in its place close to the end of the spectrum range. At this point, the particular pure element spectrum should be visible on the measurement range.

In table J are start positions for different source high-voltage settings. They provide a convenient way of starting the high-voltage (fine-)tuning, which is nearly always needed after the preliminary setting.

Table J. Start positions for high-voltage adjustment. 1st most significant, 8th least significant.

HEPS, SAPS & SUPS probes (Ar-detector)

<u>Source</u>	<u>DIP switches on</u>	<u>Check sample</u>	<u>Peak channel</u>
Cm-244	1,2,5	Fe	100
Cd-109	1,3	Fe	80
Am-241	1,3,7	Zn	73

LEPS & SLPS probes (Ne-detector)

<u>Source</u>	<u>DIP switches on</u>	<u>Check sample</u>	<u>Peak channel</u>
Fe-55	2,3	Si	75

DOPS probes (Ar-detector)

<u>Source</u>	<u>DIP switches on</u>	<u>Check sample</u>	<u>Peak channel</u>
A Cd-109	1,3,5	Fe	80
B Fe-55		Ti	100
A Am-241	1,3,5	Zn	73
B Cm-244		Fe	100

There are cases when special settings are required. Adjusting these, the following guidelines should be remembered:

- The backscatter peak should not interfere with the optimal measurement range, that is: channels 50 to 200. Note especially with Fe, Cm and Am sources.
- The channels below approx. 35 are automatically zeroed by the X-MET.

8.7 Maintenance commands

With the exception of the pre-defined function keys, all commands are entered as strings of three letters. Each command is confirmed with the CONT/YES key. The maintenance commands can only be executed in the maintenance mode, that is after the EMP command is executed. Maintenance command mode is disabled by executing the XMP command.

Should you have a dark display, adjust it with the CTRS- key. If this does not seem to help, verify that the SH is not visible on the display when adjusting. If SH is on the display, press SHIFT key, and try again.

WARNING: Certain commands should not be executed, if their meaning is not understood. The command RST resets the whole instrument and calibrations. Also, severe damage can be done by changing the memory data with ICU or MMU commands.

The commands are listed in alphabetical order, along with a short description of the task the command performs.

These commands are often referred to as e.g. EMP/PRM which on the X-MET means the following:

```
> EMP   CONT/YES
> PRM   CONT/YES
```

CHK : Warm reset

The start test resembles the power-up routine, after which "SELF TEST COMPLETED" is displayed.

CHT : Channel test

The channel test allows the operator to select different gain values in order to test the operation of the gain control correction. An internal oscillator checks the analyzer's microchannels. Therefore, the probe must not be connected.

Example of the output:

```
> EMP   CONT/YES
> CHT   CONT/YES
CHANNEL TEST
GAIN 128 ? CONT/YES   (accept the default)
MEASURING: PROBE 1 TYPE NONE
10 SECONDS
```

nnn : pulse#1 mmm : pulse#2
 0-50 : pulse#0 255 : pulse#3

>

The abbreviations for the above are as follows:

nnn = the microchannel where the first peak occurs in the spectrum (usually 100-130).

mmm = the microchannel where the second peak occurs in the spectrum (usually 177-228).

pulse# = the number of counts in the respective channel.

The correct values are 0 (zero) for pulse#0, and a max. difference of 1 (one) between the values of pulse#1, pulse#2 and pulse#3.

Replacing the default gain value with another one (between 0 and 255) should move the peak positions respectively. A change of approx. $\pm 5\%$ in the channel position should result from the use of both extreme values.

GTS : Gain test parameter output

GTS activates the output of gain control parameters. The display interval is the entered test counter value multiplied by three (in minutes), so e.g. value 1 for the counter gives parameters every 3 min. (except the first one after 1 minute), a value of 10 every 30 min. etc. The use of GTS is slightly different when an electrical distribution box is connected. Contact a representative of Outokumpu Instruments for further information.

Example of the output

```
> EMP
> GTS
GAIN TEST COUNTER: 0? 1
```

GAIN CONTROL TEST DATE: 28.02.91

Time probe gain T-value slope norm.coeff.

```
09-46-54 1 128 0.0338 250.00 1.0000
09-50-05 1 129 0.0261 456.63 1.0000
```

...

The most important value here is the GAIN value. When initialized, it is set at 128. As the conditions change, so does the GAIN value. The ageing of the detector tends to raise this value. If it reaches 255 or 0, the instrument prompts an error message: GAIN CONTROL: GAIN OUT OF RANGE. In this case, the probe must be re-initialized, and the calibrations checked, possibly recalibrated. A calibration can be saved if DIP switches are adjusted to return the reference peak to its original position. Then re-initialize, and set the Alow, Ahigh, Blow and Bhigh

values (EMP/PRP) to their original values.

ICU : Examining and changing the contents of the ICU memory

The sub-commands for examining the data are;

CONT/YES	Scroll forwards.
▲	Scroll backwards.
/aaaa	Go to address aaaa. Possible values are hex digits 0 - FFFF.
dd	Deposit dd into the memory. The memory is 8-bit, so possible data values are hex digits 00 - FF. If the deposit is not accepted, NO CHANGE will be displayed.
END/NO	Ends the function.

MMU : Examining and changing the contents of the MMU memory

The use of MMU is similar to that of ICU. Accessible memory areas are 0 - 1FFFF, 80 000 - BFFFF and FF0001 - FF3FFF. If an attempt is made to store data into the instruments program memory area, X-MET will prompt PROM ADDRESS aaaaaa dd.

PCT : Probe code test

The operating status of a particular probe can be checked using the command PCT. The command displays the probe number, type, and information received from the microswitches.

The command is used to evaluate possible microswitch faults. The proper values are as follows:

Table K. REF/IND values for HEPS, LEPS and SLPS.

Measurement base position	Probe status	Type	REF	IND
in front	gain control	010 HEPS or	0	1
intermediate*	hold	011 LEPS or	1	0
rear	measurement	100 SLPS	1	1

* The SLPS probe has no intermediate position.

Table L. REF/IND values for SAPS.

Shutter position	Probe status	Type	REF	IND
Closed	gain control	001 SAPS	0	1
Intermediate	hold	(or 101)	1	1
Intermediate	hold (open)		1	0
Open	measurement		0	0

Table M. REF/IND values for DOPS.

Shutter position	Probe status	Type	REF	IND
Closed	gain control	110 DOPS	0	1
Intermediate	hold		1	1
Open	measurement A source		0	0
Open	measurement B source		1	0

PRM : Examining and changing model parameters.

PRM displays the model GENERAL PARAMETERS, CHANNEL PARAMETERS, G MATRIX and ASSAY/IDENT PARAMETERS.

Example:

> PRM

GENERAL PARAMETERS ? P

General parameters: (MODEL 24: ZNCONC)

Type	Meas time	Channels	Flow channel	count rate	Max c.rate	Safety %
Assay	240	5	0	0.0000	6kHz	0.0000

Channel parameters: (MODEL 24: ZNCONC)

Chnl	El	Pr	S	Low	High	Peak	Norm.coeff.	Norm.int	Slow	Shigh
1	CD	4	A	196	207	200	1.0000	2959.010	0.00	100
2	AG	4	A	184	195	191	1.0000	3087.23	0.00	100
3	SN	4	A	211	222	218	1.0000	1362.550	0.00	100
4	SB	4	A	223	234	227	1.0000	2181.810	0.00	100
5	BS	4	A	255	255	255	1.0000	1008.62	0.00	100

G-Matrix: (MODEL 24: ZNCONC)

	1	2	3	4	5
1	1.197	-0.442	-0.110	-0.031	-0.011
2	-0.447	1.188	-0.013	-0.006	-0.040
3	-0.033	-0.195	1.231	-0.493	-0.017
4	-0.178	0.093	-0.464	1.208	-0.008
5	0.000	0.000	0.000	0.000	1.000

Assay parameters: (MODEL 24: ZNCONC)

Dependents:

Dependent	Name	No of indep's
1	AG	2

Functions:

Dep	f1	f2	f3	f4	f5	f6
1	AG	AG*BS				

Coefficients:

Dep	Intercept	Slope1	Slope2	Slope3	Slope4	Slope5	Slope6
1	92.9813	-5.0009	0.0047	2.2681	10.997	-14.329	7.3648

Standard:

Dep	Meas. time:	240
1	Assay	Original intercept
	754.5	92.9813

>

Some explanations: first, there are four sub-levels - general parameters, channel parameters, G-matrix and assay/ident parameters. These parameters comprise the model. Of the first ones, the flow channel, count rate and safety % are for on-line use only. The most important is the max. count rate, which can be changed by giving END/NO to 10 or 15 kHz. It sets the limit for the warning TOO HIGH COUNT RATE, with a default at 6 kHz. Always try to keep the count rates as close to 6000 c/s as possible. The model type can be assay, ident, or undef(ined), if no sample calibration has been performed, or intensity, if only PUR is completed. Meas time and channels are obvious. In the channel parameters is the pure element data, with element number, name, probe, source (A or B), lower and higher limit, the peak value, the normalization coefficient, the normalizing intensity, and two unused parameters (Slow, Shigh). The G-matrix has the information for the spectrum purification calculations. The diagonal values should be close to 1, and the BS line should have zeroes, except for the diagonal value 1.000. If larger values than 3 appear, most certainly something is wrong in the pure element calibrations. Also, the BS should have only zeroes on its line (except for the one 1.000), otherwise the BS sample is contaminated with elements in the measurement range. The assay parameters give the independents and the intercept and slope values. Note, that the slope values are not zero for nonexisting independents, but are random numbers (in example, from slope 3 onwards). In the standard is the measured assay value of the standard (see command MST/STA), with the original slope, which is adjusted after a STA measurement. Note, that in ID models the parameters contain the upper and lower threshold values, and relative ranges of elements instead.

NOTE ! Nearly all of the parameters can be altered, so be careful when typing. A very good reason has to exist in order to change these original values. Type only CONT/YES, if nothing is to be altered.

The default value for the total count rate upper limit is 6 kHz. If this is exceeded, an error message COUNT RATE TOO HIGH is displayed. The limit can be extended to 10 or 15 kHz individually for each model. It should be understood, however, that this is not in accordance with the optimum measurement conditions. Therefore the use of limiter rings or filters should be the primary action in case high pulse count rate values are discovered (except in alloy applications).

PRP : Examining and changing probe parameters.

This provides access to several parameters concerning the probe in use, especially

to gain parameters. Example:

> PRP

PROBE NUMBER: 1 ? P (CONT/YES, P for list)

Probe	Type	Mode	Norm.mode
1	SAPS	INI	MANUAL
2	HEPS	INI	MANUAL
3	LEPS	INI	MANUAL
4	SLPS	INI	MANUAL
5	DOPS	INI	MANUAL
6	NONE	UNINITIALIZED	AUTO

Probe number: 1 ? (CONT/YES)
GAIN PARAMETERS ? P (CONT/YES)

Gain control parameters:

Probe	Alow	Ahigh	Blow	Bhigh	T0	Slope	Gain	Scout	Mode
1	80	94	65	79	0.01189	484.74	132	4	INI

Normalization parameters :

Probe	Coefficient	Low	High	Intensity	Mode
1	1.00000	69	91	980.22	MANUAL

Probe parameters:

Probe	Type	Model	Reference	Resolution	B/A ratio
1	SAPS	1	BS	0.00	1.000

GAIN PARAMETERS ? (END/NO, if no manipulations)
NORMALIZATION PARAMETERS ? END/NO
PROBE PARAMETERS ? END/NO

>

The parameters are as follows: first we got a list of all probes and their types with P after the first PROBE NUMBER: 1 ? prompt. Then we got a printout of the actual parameters with P after GAIN PARAMETERS ?. The parameters Alow...-Bhigh are gain control channel limits. T0 and slope are used in the calculation of the gain value. Gain is the gain value, set to 128 at INI. Scout is for on-line applications, and INI is the initialization mode.

NOTE! You can accidentally change the INI to ING mode by giving END/NO at that point. Be sure to give CONT/YES, ING is for on-line measurements only. The same thing can happen at next line: MODE: MANUAL, which can change to AUTO, if END/NO is pressed.

The probe parameters include Reference and Resolution, which can be entered. The B/A ratio is for the DOPS probe measurement time ratio between the two sources, default is 1.000. It is a good precaution to take a printout once in a while of the PRP command.

RST : Cold reset (total reset)

The cold reset is used to erase all the stored information in the instrument. It returns the analyzer to its initial state, and certain checksums are counted from the system area. The reset is confirmed with CONT/YES key after the prompt TOTAL RESET?

After RST the analyzer is in the following state:

- * All probes are uninitialized.
- * Measurement time is set to 15 s.
- * Model 1 is in use.
- * The calibration table is empty.
- * Reference table is empty.
- * All models uncalibrated.
- * Spectrum table is empty.

As RST destroys all the information stored by user, it should not be performed without a compelling reason.

RWM : Read/write memory test

RWM runs a built-in test on the system read/write memory. The test does not alter the contents of the memory. After a successful test, TEST COMPLETED will be displayed. Possible error messages give information on the location of the fault.

TAO : Test analog output

A sawtooth wave of 5 V/3 ms will be transmitted through the analog output. The test is finished with the END/NO key. An oscilloscope will be needed.

TSI : Test serial interface

TSI runs a built-in test on the serial interface. For this a special test plug (code 3877 404) into the IN/OUT connector is required, or by short-circuiting the serial cable's pins 2 and 3 in the D-25 connector (after prompt CONNECT TEST CABLE AND PRESS CONT). After all the communication speeds have been tested, a message TEST COMPLETED is displayed.

TSM : Test measurement

TSM performs a normal measurement for either a sample (probe in the measurement position) or the gain control reference material (probe in the gain control position). After the measurement is completed, the peak channel, peak channel count value and the FWHM (Full Width at the Half Maximum of the peak) are displayed. During the measurement the gain parameter value is constantly 128. This enables the user to make a test measurement irrespective of the probe status, i.e. uninitialized probes can be used. Use command SS2 with the DOPS probe to select the lower energy source (source B). From the FWHM, the peak channel and the sample identification data the probe resolution can be calculated.

The resolution is calculated as follows:

$$RES(Mn K) = 100\% \times \frac{FWHM}{PEAK CHANNEL} \times \sqrt{\frac{E(element) keV}{E(Mn K)}}$$

Also, this command is handy in evaluating the highest count rate from the calibration samples before commencing the sample calibration. Measure the sample with the highest concentrations with 10...20 s with EMP/TSM and then give TCR to get the count rate.

XMP : Inhibit maintenance mode

Inhibits the maintenance mode. To re-enter the maintenance commands, EMP has to be entered.

9. TROUBLESHOOTING

9.1 Unsatisfactory operation

The problems associated with the use of the analyzer can roughly be divided into two groups:

1. The analyzer gives poor results, or
2. The analyzer does not operate.

In the case of an error, the user is informed with one of the X-MET error messages. These are covered in sect. 9.2. If a malfunction is suspected but no particular error message is displayed, the following simple troubleshooting procedure may prove to be helpful. If satisfactory operation cannot be restored, contact the nearest representative of Outokumpu Instruments.

9.1.1 Poor measurement results

If the analyzer gives poor results, the following checks are to be carried out:

1. Make sure that the analyzer has been operated according to instructions, and that:
 - the sample cup is properly inserted, or the sample covers the probe aperture
 - the analyzer has been allowed to stabilize for about half an hour and to carry out gain control for 5 minutes,
 - the temperature variations have been within a few degrees during the last 10 minutes,
 - the sample cup holder and measurement window are clean,
 - the probe plug is well inserted into the electronic unit (push firmly).
2. Make sure that the poor results are not due to statistical errors. Measure the sample several times. If the results fluctuate, this is probably due to statistics, or the sample is out of the calibration range, there are superfluous independents in the model or they are too complex, or there is a gain control problem. The statistical error is reduced if longer measurement times are used. Drop independents with too

small t-values, and check from the sample intensities the concentration range by comparing to the CIN output of calibration sample intensities.

3. If the errors are not of statistical origin, the probe or analyzer parameters may have drifted. In this case it is possible, that the probe initialization or sample calibration has been performed in instable or improper conditions. Check the value of the GAIN parameter with EMP/PRP or EMP/GTS to check the detector. Have any error messages been displayed? See error messages. If there is notable fluctuation in the probe gain values, e.g. 10 units in a short (ca. 10 min) time, electrical instabilities can be suspected, and professional repair is needed. Re-initialize the probe (sect. 5.1.4), if the GAIN value is 255 or 0. Recalibrate the models for the probe in question. Do not use old pure element spectra. A calibration can be saved if DIP switches are adjusted to return the reference peak to its original position. Then re-initialize, and set the Alow, Ahigh, Blow and Bhigh values (EMP/PRP) to their original values.

4. Check, that the normalizations (NOR) have been performed according to the table in chapter 4. Check, that the normalization coefficients are sensible (should be 2.000 after one half-life time of the source). Also, if a standard sample has been measured after the calibration with MST, a standard sample correction STA can be made with the same sample.

5. Should the results still remain poor, it is possible that the pure element or sample calibration has been improper or insufficient, and a new calibration is to be carried out.

Check, that the tested sample concentrations are within the limits of the calibration samples - for all major elements. Before calibrating, it is advisable to check the resolution of the proportional counter in the probe. Should it exceed the acceptable values, the detector or the probe electronic are malfunctioning. Contact a representative of Outokumpu Instruments. For the calculation of the probe resolution, refer to sect. 9.1.2.

6. The location of the peak center also contains information on the behavior of the proportional counter. If the peak has shifted by more than 10 microchannels, the probe has to be re-initialized, and all calibrations associated with the probe must be renewed (see item 3 on this list). The high voltage supply of the detector must be adjusted or possibly the detector replaced in order to restore proper operation. For further instructions contact a representative of .

7. The total count rate should be between 1500 and 6000 counts per second. The optimum is usually about 3000 counts per second. The total count rate can be obtained by the TCR command, e.g. by giving EMP/TSM, measuring for 10 s, and then giving TCR. Also the reference can be checked this way.

If the count rate is too high, the user should reduce it by limiting the area of the sample "visible" to the radiation with a limiter ring (an X-MET accessory). If the limitation is wished to be permanent, refer to sect. 8.5 for filter (absorber) installation.

If the count rate is too low, the radioactive source is too weak and should be replaced, or possible filters should be removed (sect. 8.5). Contact a representative

of Metorex Inc. Also, the gain control may not work correctly due to too small count rate from the reference (especially Fe-55 and Cd-109 sources). Contact your local representative for repair.

8. If the above mentioned procedures are not sufficient, the user is most probably facing a major hardware malfunction and the instrument needs professional service. Contact a representative of Metorex Inc.

9.1.2 The probe resolution

The probe resolution reflects the operational status of the proportional counter (detector) and its associated electronic. An increased resolution value means decreased peak detection accuracy. The resolution is calculated from the FWHM (full width at half maximum) - peak channel ratio; for a spectral peak of Mn in channel 90 and FWHM of 14, the resolution is $14/90 = 0.1555$ or 15.6 %. The probe resolution must not exceed 18 % when calculated at the Mn K_α-line.

Since the peak resolution is inversely proportional to the square of the particular spectral line energy, the probe resolution can be evaluated from other samples too. For the line energy values see tables A and B in sect. 2.3. The resolution formula is presented in sect. 8.7. under TSM command.

Example: Calculating the probe resolution from a Si-K_α-line.

```
> EMP
> TSM          (insert Si pure element, place probe in measurement position)
MEASURING: PROBE 4 TYPE LEPS
100 SECONDS LEFT...
```

```
PEAK CHANNEL : 75      COUNTS : 3750
FWHM : 20 ( 65 - 84 )
```

From table A (ch.2) we find the following values:

```
E (Si,Kα) = 1.7 keV
E (Mn,Kα) = 5.9 keV
```

From equation (10) we have:

```
ResSi = 20/75 x 100 % = 26.7 % (100 % * FWHM/Peak channel)
```

$$Res_{Mn} = Res_{Si} \times \sqrt{\left(\frac{1.7}{5.9}\right)} = 0.2667 \times 0.5368 = 14.3\%$$

Notice the diminution of the apparently large resolution value.

9.1.3 The analyzer refuses to operate

If the analyzer does not start, the first thing to do is to check that the connection between the

analyzer and power supply is correct (sect. 3.3) and that the battery is charged and in condition. Check the main fuse, which is located in the back of the electronic unit behind the battery pack. If the fuse is to be replaced, the substitute should be of the type 5*20 mm 0.5 A slow-blow. Another fuse is in the charger unit, see chapter 3.

If the user has several electronic units/chargers/battery packs, it is advisable to try several combinations, so that the possible power supply malfunction could be located.

Also, if the keyboard refuses to work, give command UNL to (possibly) unlock the keyboard. If the display does not show anything, but audible signals can be heard, adjust the contrast with the CTRS+ -key. If this does not help, the LCD is malfunctioning. Test this with a terminal.

Contact your Metorex Inc. representative, if no response is received.

9.2 Error and warning messages

The error messages and warnings included in the operating software are listed below, as well as the action to be taken by the operator in each case. If some other error message is displayed, make a careful note of it and the situation and contact the nearest representative of Outokumpu Instruments.

Before switching OFF, the run of commands has to be stopped by entering END/NO, so that the prompt > can be seen at the start of the line. Otherwise the error message MODEL PARAMS CHANGED, PURE EL. SPECTRA CHANGED, REFERENCE SPACE CHANGED or GAIN CONTROL PARAMS CHANGED may appear after the next ON switching. In that case the message can be acknowledged with the CONT/YES key. The error will disappear after rerunning and terminating the incorrectly interrupted command and by writing in the changed parameters, like channel limits, gain control channel limits, regression parameters etc.

XX ALREADY GIVEN

The element of this name (XX) has already been measured with the same probe. Check the element symbol entered and the pure element sample. X-MET will prompt for a new pure element symbol. By entering it the calibration can be continued. END/NO will terminate the calibration.

BATTERY LOW

The battery voltage is low. Power will be switched off without further warning in about half an hour. The function that was interrupted by this warning can be completed by acknowledging the warning with the CONT/YES key.

The battery must be connected to the charger or replaced with one of a full charge. The analyzer can be used during charging. To replace the battery, first switch off power with the OFF key. When restarting, observe the proper stabilization and gain control time. To avoid getting the battery into a "deep discharge" state, if auto power-off is done, the battery should be disconnected and charged as soon as possible - either with or without the instrument.

CALIBRATION DATA IN MODEL n

The calibration measurements were made with model n and not with the current model. The calibration data can be manipulated only in the latest model.

Switch to model n (MODEL key) or make calibration measurements for the current model (PUR, CAL).

CALIBRATION TABLE CHANGED

The intensities in the calibration table have changed. Most probable reason is incorrect OFF-switching during CAL or CIN without terminating the run of commands by END/NO. The message can be acknowledged by CONT/YES. The erroneous condition may disappear after restarting CAL, CIN or ASY, and terminating them by END/NO. Should data in CIN or ASY have changed, type in the original values, if available. If this does not help, a new sample calibration is needed, if the intensities of the calibration table are still needed for calculation of new regression models (MOD). If the error occurs repeatedly, the analyzer needs repair.

CALIBRATION UNFINISHED

The calibration of the current model is unfinished. Complete the calibration (Chapter 5).

CONNECT PROBE FIRST

The probe has not been connected to the electronic unit. Switch the power off, and plug firmly the probe cable into the PROBE connector, then switch the instrument on again.

COUNT RATE TOO HIGH: XXXX

The total count rate (XXXX) exceeds the specified count rate limit (see PRM). The message is displayed after the first second of measurement. The operator can continue, start again or stop the measurement by pressing CONT/YES, START or END/NO to the prompt CONTINUE?, if the total count rate was under 15 000 c/s. If it was higher, the instrument will automatically terminate the command. The message is a warning about a potentially distorted spectrum. Reduce the count rate (sect. 8.5 and 9.1.1). If a sample is measured, then the message is a warning of working out of the calibration range.

COUNT RATE TOO LOW: XX

The total count rate is less than 64 counts per second.

The pulses from the probe are not reaching the electronic unit. Check that the probe is properly connected. The probe must be allowed to stabilize for a while after the instrument is switched ON before it begins to issue pulses. Notice that measurements of the highest accuracy cannot be made until after a stabilization interval of half an hour. The error message may also be a symptom of a broken cable, a loose or a dirt-covered source, an exhausted source, a detector fault, or a

faulty FET on the RPAU board of the probe.

GAIN CONTROL: GAIN OUT OF RANGE

The computed gain value is outside of the permissible range. Ensure that proper initialization has been performed for the probe. Check gain value with EMP/PRP command. The error message is a symptom of strong drifts in the spectrum. The gain value has exceeded 255 or 0, and the instrument will not perform any further gain control for this probe. The probe must be re-initialized, and a new pure element calibration must be performed, possibly also a new sample calibration. If the time elapsed from the initialization of that probe is less than 6 months (for a new detector) it is replaced under warranty. Generally, if less than 4 months has elapsed from the latest INI, the detector should be replaced.

Restart the analyzer through the OFF-state, let it stabilize in the measurement position, and then let it perform gain control for a minimum of 5 minutes. If the erroneous condition reappears perform a new calibration for that probe starting from the gain control initialization (INI). **NOTE:** Refer to the calibration recovery procedure in chapter 9.1.1.

GAIN CONTROL PARAMS CHANGED

The parameters of gain control have changed. The reason can be incorrect OFF-switching during previous INI or PRP. The run of either of these commands has not been terminated by END/NO. In this case the error condition can be acknowledged by CONT/YES. The condition will disappear after rerunning the unterminated command, and typing in the changed data with PRP; first let the instrument do gain control for ca. 1 minute. If data is not available, a new instrument calibration is needed (INI, PUR). It can also be a symptom of an exhausted backup battery. If the error occurs often the analyzer needs repair.

GAIN CONTROL: TOO BIG GAIN CHANGE

Proceed as for the error message: GAIN OUT OF RANGE.

GAIN CONTROL: TOO BIG SLOPE

During the gain control cycle, the value of the gain control slope has been abnormally large. Ensure that the ambient conditions have been normal and within permissible limits. Check gain value with EMP/PRP, to ensure that gain is not out of range.

The error message might be a symptom of drifts in the spectrum. Let the instrument do gain control for a time of at least 5 minutes. If the error reappears, proceed as for the error message: 'GAIN OUT OF RANGE'.

NOTE: Some error messages concerning GAIN CONTROL may be due to contamination of the detector or source by dirt, sample, loose source etc.. Contact your local Outokumpu Instruments representative.

INITIALIZATION INTERRUPTED

The gain control initialization measurement has been interrupted by pressing END/NO or by moving the reference (by opening the shutter). Position the probe in the

gain control position and restart initialization (INI).

INPUT ASSAYS FIRST

The concentrations of the calibration samples have not been entered, before starting the MOD command. Enter the concentrations with the ASY command.

LATEST SPECTRUM CHANGED

The latest measured spectrum has changed. Remeasure the sample.

LIBRARY MEMORY FULL!

The reference library memory is full. A total of 400 references can be included in the identification library calibration.

MAKE A NEW MEASUREMENT

When calculating results with a model calibrated for several probes, or both sources in DOPS, only the last measured spectrum is in the instrument memory. A new measurement has to be performed.

MATRIX INVERSION ERROR

The determinant of the instrument matrix calculated during calibration is close to zero. Check the pure element samples (that no pure element sample was measured twice) and renew an incorrect pure element calibration (PUR). Remove possible overlapping element channels, a normal cause, e.g. with As and Pb pure elements, by manually setting the limits (LIM). If the error is repeated, the analyzer needs repair.

MEASURE CAL. SAMPLES FIRST

Fewer than two calibration samples have been measured. Measure more calibration samples. Refer to Chapters 4 and 5 for recommended minimum number of samples.

MEASUREMENT INTERRUPTED

The measurement has been interrupted because of shutter movement, disconnection of the probe, or by pressing END/NO. To connect the probe, first switch power off with the OFF key. After power-up, let stabilize and start a new measurement. This can also be a symptom of misaligned or malfunctioning microswitches in the probe, which prevent the measurement from beginning.

MEASURE PURE ELEMENTS FIRST

The pure element calibration has not been done. Carry out pure element calibration (PUR), but first ensure that the other steps of instrument calibration have been completed: (see sect. 5.1). If the initialization (INI) has been performed earlier, it should not be renewed.

MICROCHANNEL OVERFLOW

Overflow of the counts in a microchannel. Over approx. 16 million pulses have been attempted to store in a single microchannel. Use a shorter measurement time.

MODEL PARAMS CHANGED

The parameters of the current model have changed. Check the operation of the model, and the model parameters with EMP/PRM command (pure element limits, G-matrix, independents, assay values, standard values). Perform instrument calibration for the faulty model if data has changed, and check the model data entered (ASY). The error message can first be acknowledged with the CONT/YES key, after which operation can be continued just for checking. This can be a symptom of a discharged or faulty backup battery.

NO CAL. SAMPLES IN MEMORY

The calibration table in memory is empty. Start by measuring calibration samples (CAL).

NO DEPENDENTS IN THIS MODEL

The model generation is unfinished: dependent variables, i.e. elements whose concentrations are desired to be calculated have not been entered in sample calibration, with command ASY. Finish the sample calibration, see Chapter 5.

NO INDEPENDENTS GIVEN

No independent variables have been defined in model generation. Start model generation with MOD command and enter independents (see sect. 5.3.4)

NO REFS IN THIS LIBRARY

There are no references in an identification model. Measure references with the ADD command (see sect. 5.4.1)

XX-PEAK SHIFTED OVER 5%, OK?

A note, that the peak of element XX has shifted in pure element recalibration. Check that you have measured the correct pure element samples in the correct order. CONT/YES accepts the change, END/NO rejects the new measurement. The message may also be a symptom of electrical instability or a detector leak. Contact the nearest X-MET service agent, if repeated, and/or peak has really shifted.

PEAK TOO NEAR SPECTRUM ENDS

The peak of the gain control reference is too close to the extreme ends of the spectrum; the limit for the peak channel is < 20 (bottom) or > 254 (top). The peak position can be shifted by altering the high voltage or by selecting another element to be used as the reference (Fe-55 source).

PURE ELEMENT SPECTRA CHANGED

The pure element spectra in the spectrum table have changed. Most probable reason is incorrect OFF-switching during the previous command which has referred to the table (LIM, PUR). The run of the command has not been terminated by END/NO. In this case the error condition can be acknowledged by CONT/YES. The condition will disappear after rerun of the terminated command, and by typing in the old values for the parameters (channel limits, norm. intensities). If of no help, a new pure element calibration must be performed. If the error occurs often, the analyzer needs repair.

REFERENCE SPACE CHANGED

The intensities of identification standards have changed. Most probable reason is incorrect OFF-switching during ADD or REF without terminating the run of commands by END/NO. In this case the message can be acknowledged by CONT/YES. Check reference names, thresholds etc. The erroneous condition will disappear after re-entering ADD or REF and terminating them by END/NO, and by remeasuring reference samples (ADD). If the error occurs often, the analyzer needs repair.

REF NAME ALREADY EXISTS

A reference bearing this name is already in the system memory. Give the reference another name, unless you are doing a calibration for the AUTOSCREEN mode.

REGRESSION ERROR: CHECK INDEPS

The determinant of the matrix calculated during generation of the regression model is close to zero. Check whether the independent expressions are sensible. This error may occur if all the independent expressions have strong mutual correlations. In this case, reduce the number of independents.

THIS IS AN ASSAY MODEL

The model has previously been defined as an assay model. It can be changed to an identification model by deleting it with the DEL command and then making a completely new calibration.

THIS IS NOT AN ASSAY MODEL

The model is an identification model, or no calibration measurements (CAL) have been made. In the latter case, if it is desired to enter parameters with the PAR command without making sample calibration measurements, make a brief excursion to the CAL function as follows:

```
> CAL  
NO OLD DATA  
MEASURE SAMPLE 1 END/NO  
LAST SAMPLE 0? CONT/YES  
>
```

The model is now designated as an assay model, and parameters can be entered without measuring the calibration samples. If the model is already marked as an identification model it can be marked as an assay model by deleting it with the DEL command and then making a completely new calibration, or with EMP/PRM command at "model type" point: an END/NO changes the model type.

THIS MODEL IS A LIBRARY

The model has been previously defined as an identification model. It can be changed to an assay model by deleting (DEL) and making a completely new calibration. See also previous message.

THIS MODEL IS NOT A LIBRARY

The model has been defined as an assay model or its type is undefined. An undefined model can be defined as an assay model by the CAL command or as an identification model by the ADD command. If the model is already defined as an assay model, it can be changed into an identification model by deleting it with the DEL command and then making a completely new calibration, or by changing "model type" under EMP/PRM.

THRESHOLDS IN WRONG ORDER

The value of LOWER threshold is higher than the value of UPPER threshold. Give new values by THR, default values are under command THD.

TOO MANY INDEPS FOR THESE POINTS

The number of calibration samples is too small for the number of independents used. Reduce the number of independents or measure more calibration samples (CAL). Refer to Chapters 4 and 5 for recommended minimum number of calibration samples.

UNCALIBRATED MODEL

The model has not been calibrated. Carry out calibration (see Chapter 5).

WARNING! 2 VERY CLOSE PEAKS

The separation between some peaks is less than a quarter of the channel width. This is usually the result of repeated measurement of the same pure element. If this is the case, start pure element calibration from the beginning (PUR). If the reason is bad statistics use a longer measurement time. If the closeness of the peaks is accepted, the channel limit will be set at the half-value points of the peaks, and the channels overlap reduces the identification accuracy. If desired, the channel limits can be checked with a printer/terminal, and changed with the LIM command manually.

10. SUMMARY: X-MET 880 COMMANDS

Operator input	Description	Page
CTRS+ /CTRS-	Adjust LCD contrast	28
START	Start a measurement	82
MODEL	Select a (new) model	82
M.TIME	Select a measurement time	82
RECALC	Recalculate a measurement	82
F1...F5	User definable functions	83
***	Comment, no X-MET response	87
ADD	Add a reference sample to the library	73
AMS	Mean value of several measurements	83
ASY	Define dependents and enter assay values of calibration samples	58
BLT	Toggle display backlight on/off	83
CAL	Measure calibration samples	57
CAO	Configuration of the analog output	83
EMP / CHK	Warm reset (selftest)	94
/ CHT	Channel test for gain control check	94
CHR	Send ASCII code text to the serial interface	84
CIN	Display calibration sample intensities	58
CMG	Continuous measurement w. gain control (on-line)	84
CMS	Continuous measurement	84
CSI	Configure the serial port	85
DEL	Delete a model	85
DTM	Display time and date	85
EMP	Enter maintenance mode	94
FNC	Program function keys	83
FPI	Pass/fail identification	76
FRQ	Set check count rate (on-line only)	-
/ GTS	Gain test	95

Operator input	Description	Page
HLP	List of X-MET commands to terminal	85
/ICU	Examine ICU memory	96
ING	Initialization for on-line measurements	-
INI	Initialize a probe	40
INT	Display channel intensities	85
LIM	Examine pure element channel limits	55
LOC	Lock keyboard	85
MDE	= MODEL, choose a new model = <Ctrl>-D	86
/MMU	Examine the MMU memory	96
MOD	Regression modelling	59
MST	Measure standard sample into instrument memory	79
MTM	Set model measurement time (default)	86
NOR	Normalization of model manually	77
PAR	Enter model parameters manually	64
/PCT	Probe code & microswitch operation test	96
POF	PC command off (parameter dumping)	-
PON	PC command on (parameter dumping)	-
/PRM	Parameters of the model	97
/PRP	Parameters of the probe	98
PUL	Display channel gross count rates	86
PUR	Pure element calibration	49
REC	= Recalculation = RECALC = <Ctrl>-R	86
REF	Examine, rename or delete reference samples	74
/RST	COLD RESET = TOTAL RESET	100
/RWM	Execute read/write memory test	100
SEQ	Set sequence for CMS/CMG	83
SPE	Spectrum channel intensity output	52
SPL	Spectrum plot to terminal	53
SPR	Select probe	32
SS2	Select source 2 in DOPS (= source B)	100
STA	Measurement of standard to adjust model	79

Operator input	Description	Page
STD	Display standard deviations	86
STM	Set time and date	86
STR	=START = <Ctrl>-A	86
/ TAO	Test analog output	100
TCR	Total count rate	86
THD	Examine ID threshold default values	75
THR	Examine/change ID threshold values	75
TIM	= M.TIME = <Ctrl>-T = Set current measurement time	87
/ TSI	Test serial interface	100
/ TSM	Test measurement (of sample or reference)	100
UNL	Release keyboard lock	85
/ XMP	Inhibit maintenance commands (EMP)	101

Commands in bold are maintenance commands executable only after command EMP.

11. APPENDICES

HOW TO DEVELOP THE BEST POSSIBLE ASSAY MODEL

1. BASIC THEORY

The X-MET uses the so called empirical calibration approach, that is the calibration equations are developed based on intensities measured on known calibration samples. The general calibration formula is patterned after the intensity correction model of Lucas-Tooth and Price. The generalized calibration equations for the analyte I in a sample can be written as follows:

$$C_i = I_i \cdot (K_i + \sum_{j=1}^n (K_{i,j} \cdot I_j)) + B_i + \sum_{j=1}^n (B_{i,j} \cdot I_j)$$

TERMS: 1 2 3 4

As can be seen, the model assumes that the analyte concentration is the function of intensities of elements in sample. While this model is limited to relatively narrow concentration ranges, it has an important advantage that only the assay of the analyte are required to develop it.

Let us note that if no matrix effects are present in sample, the calibration equation would have only part 1 and 3, and would be that of the regular straight line.

The second term modifies the slope of the calibration line, according to the amounts of either elements as determined by their intensities. This correction is needed when the matrix element is close in energy to the analyte, so that it strongly absorbs or excites its radiation. It is also useful when the matrix element varies over such a large concentration range itself that it significantly changes the effective matrix absorption of the incident or emitted x-rays. The square term, $I_j \cdot I_j$, would be the correction for self absorption.

The fourth term reflects the change in background intensity under the analyte peak. This term is significant if matrix element(s) vary enough to alter the matrix scattering power to change the general shape of the background, or more commonly, if the matrix element has a peak that overlaps the analyte peak. The overlapping peak may also be an escape peak. This situation often arises in alloy analysis where strong peaks of iron, chromium, or nickel can produce escape peaks 2.9 keV left to their fluorescent peaks (*caused by argon filling*).

2. PARAMETERS USED IN REGRESSION MODELING.

R- COEFFICIENT OF CORRELATION. It tells how well the given calibration equation explains the variation of data. Its value varies between 0 and 1. The closer its value to 1, the better the calibration model is. It should have a value greater than .65 to be meaningful. It is a function of the number of independents, the number of data points, and usually increases as those numbers increase.

NOTE: This coefficient alone, however good, cannot be a basis of the goodness of the model. Often in the case of limited number of data points and over complicating the calibration equation, one can get a "perfect" $R = 1.000$, which, however, is meaningless.

S - STANDARD ERROR OF THE FIT. Also known under the terms of Sum of Squares for Error (*SSE*), or Root Mean Square Error (*RMS*). This is one standard deviation of the spread of data points around the fitted calibration line. The greater its value, the more scattered the data points. If two lines are drawn around the calibration line at plus *S* and minus *S* distance from it. The band will be created around the calibration line in which about 68% of all the data used will fall in. The value of *S* is expressed in the units of the dependent variable being fit. During the modeling one should try to minimize this parameter.

F - TEST VALUE. This is a statistics which is expressed as the ratio of the sum of squares explained by the given regression model to the sum of squares not explained by the model (*our familiar parameter S*). If its value is low, say 5 to 10, then the model is not reliable, and may not be stable if the different data set is used for its calibration. Assuming that an average calibration set has 10 samples, the value of the *F* statistics should not be smaller than 10 for us to say with 95% confidence that the given model is a valid one. *F* is a function of the number of data points, the number of independents and *S*. It usually decreases if the number of variables increases. It is a dimensionless number.

t - TEST VALUE. This statistics is a measure of significance of the given calibration slope. It is expressed as the ratio of the slope value to the estimate of error of that slope. So, for example, *t* equal to 10 means that the error of the estimate of the slope is one tenth (*or 10%*) of the slope itself, which is not bad at all. For an average case of ten calibration samples the absolute value of *t* should not be smaller than 2.5 for us to say with 95% confidence that the given slope is statistically valid. Therefore, the rule of thumb would be to eliminate from the model all independents featuring the *t* value less than $|2.5|$. The *t* is dimensionless number and has the same sign as its slope.

STDEV - STANDARD DEVIATION DUE TO COUNTING STATISTICS. This is the error caused by the random nature of radioactivity. It is, by definition, equal to the square root of the total number of counts accumulated within the given period of time. Alternatively, standard deviation if intensity I is equal to the square root of intensity divided by the square root of the time the intensity was measured for. It is seen that by extending the measurement time by a factor of 4 one can reduce the standard deviation of counting by a factor of 2. This error is the only one easily controlled.

3. ITERATIVE PROCESS OF BUILDING THE MODEL

STEP 1. Start always with the intensity of the element of interest as the first independent variable. Next, depending on the nature of the sample matrix, try intensity of the analyte ratioed to the intensity of the backscattered radiation (*BS*). This usually works for sulfur in oil, chlorine in oil, metals in soil, or any element in light (*or highly scattering*) matrix. If the analyte range is relatively wide (*such as several percent*), try the square term of the analyte intensity (*example: tin in oil in the range of 0 to 8%*). For each regression note the values of R , S , and F . The goal is to **MINIMIZE S** as this parameter is closely related to the accuracy of the method. It can be shown mathematically that R and F are functions of S . Therefore, by concentrating on S we usually drive R and F in a right direction, that is high. Save the regression which yields the smaller S . However, have in mind that two values of S , for example one .12 and another .11, **ARE FOR ALL PRACTICAL REASONS THE SAME**. The difference between the S 'es should be at least about 20% to be a criterion for selection. If the S 'es are similar then select the model with the higher F and/or the higher R .

Examine the table of residuals. Make note of the points which are clearly off. The last column of the table tells how many S 'es below or above the curve the given point is. About 68% of the data points should have the last column value smaller than the absolute 1, 95% smaller than the absolute 2, and 99.9% (*for practical reasons all points*) smaller than the absolute 3.

Here is a worked example:

Total number of data points is 17 (17 samples). Therefore, about 12 points ($.68 \cdot 17 = 11.56$ or 12 points) should have the last column value between -1.0 and +1.0.

About 16 points ($.95 \cdot 17 = 16.15$ or 16 points) should have the last column value between ± 2.0 and ± 2.0 . This also means that 4 points should fit between -2.0 and -1.0 and between +1.0 and +2.0.

At the most, only one data point should have the absolute value between 2.0 and 3.0.

The number of points in each band may vary at least by one from the predicted number due to randomness.

If any point is distant by more than $\pm 13 \cdot S$ from the line, it becomes the candidate for deletion. However, the reason for deviation should be established first. Often it is the erroneous entry of the referee assay for this point. Sometimes it just may be a bad measurement which can be easily corrected by remeasuring the sample(s). It may also be the case of the sample being incompatible with the rest of the set. If all of the information indicates that none of the above applies, then it is probably good to delete the point and redo the whole regression. If deleting the 'outlier' results in significant improvement of the model, then usually it is justified.

Often all data points will be within the $\pm 13 \cdot S$ band, but more of them than expected will exhibit large deviations from the line. Examining the composition of those samples which deviate too much may reveal that they contain significant amounts of the other element(s) which was (were) not yet accounted for in the model. This situation provides a hint as to which independent to include in the next round of the modeling process. Examine the table of residuals and the plot of the data. Is any point or group of points indicating the curvature of the calibration line which could be corrected by including in the model a square term?

STEP 2. Now is the time to add to our first independent term the next one. It may already be obvious what to do from the examination of the table of residuals as mentioned in STEP 1 above. However, there are some guidelines to keep in mind too. The matrix element of the highest concentration should be examined by including its intensity in the model as the next variable. If that element happens to be close to the analyte peak, as is the case in alloys, then the nonlinear term in the form of the product of the analyte and interfering element intensities may prove to be helpful. Check again the S, R, and F values. If the S does not improve the independent should be rejected and the other one tried. To assess progress in reducing the S parameter, it is convenient to use the ratios of S'es and F's from the two models. If one model is better than the other one then:

$$F_{\text{better}} / F_{\text{worse}} > (S_{\text{worse}} / S_{\text{better}})^2,$$

where "better" refers to the smaller S value.

Examine the table of residuals and the plot of the data. Examine the t test values of the slopes. Reject independents) which show t smaller than ± 2.5 .

Exit the modeling and press the STD command. The X-MET should still have in its buffer memory the spectrum of the last calibration sample. Therefore, it should output on the display the values of the standard deviations due to the counting for all of the already modeled elements. Check and make a note of those STD's. They cannot be larger than the S error(s) obtained during modeling. If that is the case than the model is over corrected and should be changed by rejecting the variable with the worst t value. The S error, by definition, includes the STD, and cannot be smaller than any of its components.

Continue iterative process of modeling by repeating STEP 2 until no further improvement seems feasible.

4. CONCLUDING REMARKS

Select as the final model the one with the best (*smallest*) S. If two models have very similar S, select the one with greater value of F. If by including in the model one more independent, only a small improvement of S is obtained consider to keep the model with the larger S but with smaller STD. In most cases the smaller the number of independents in the model, the better smaller the STD value.

Use common sense. Remember that simpler is better. It is always easier to correct or knowingly change the model which has the smaller number of parameters. Do not overcorrect. If the number of calibration samples is small, it is just not possible to develop a good model. The rule of thumb is that if you fit the equation with k independents the number of samples in the model should be at least twice as much, that is $N \geq 2 * k$. If the calibration set has only 6 samples and you fit the calibration equation with 5 terms, then you will get a "perfect fit" with $R = 1.00$, $S=0.000$ and $F=****$. However, this will the yield calibration equation which will not work at all. This is the case of over defining the model on the grounds of statistical analysis.

As a rule, do not include as independents those intensities whose element concentrations in samples are very small compared to the concentration range of the analyte.

As always, there are some exceptions from the rules we tried to spell out above. One of the most significant ones is the calibration for the element which is very strongly affected by the presence of all matrix elements. A classical example is the absorbed by calcium, silica, potassium, sulfur, all present in the sample in quantities that call for all these elements to be included in the calibration. Usually, for that calibration the t values of all of the slopes are quite marginal. However, none of the variables can be rejected without significant degradation of the model parameters.

When testing the final model for accuracy, keep in mind when comparing the measured values to the given ones that if the difference seems too large, perhaps the measured sample was also off during the calibration and modeling. Therefore, we should compare the measured result with the value obtained during modeling rather than with the given one. If the difference between the S value and STD value (for the same measurement time) is significant, then the S error should be used for judging any discrepancies between the measured and the give values. That applies if S is about twice the corresponding STD.

Stan Piorek
05-23-90
Metorex Inc.
215-741-4482 X105

Chemical Resistance of Polypropylene

Substance	Temperature°C	Effect
Acetic Acid, Glacial	60 C	B
Acetic Acid, 50%	60 C	A
Acetone	60 C	B
Acetophenone	20 C	A
Ammonia, 30%	20 C	A
Ammonium Hydroxide, 10%	60 C	A
Amyl Acetate	20 C	B
Amyl Alcohol	60 C	B
Amyl Chloride	20 C	C
Aniline	60 C	A
Aqua Regia	20 C	B,E
Aviation Fuel	20 C	B
Benzene	20 C	B
Benzyl Alcohol	60 C	A
Brine	60 C	A
Bromine, Aqueous	20 C	C
Calcium Hypochlorite, 20%	60 C	B
Carbon Disulfide	20 C	B
Carbon Tetrachloride	20 C	C
Chlorine Gas	20 C	D
Chlorobenzene	20 C	C
Chloroform	20 C	C
Chromic Acid, 50%	60 C	A,E
Cyclohexanol	60 C	B
Cyclohexanone	20 C	B
Decaline	20 C	C
Detergents, 2%	100 C	A
Ethyl Acetate	60 C	B
Ethanol	60 C	A
Ethylene Glycol	60 C	A
Ethyl Ether	20 C	B
Formaldehyde	60 C	A
Gasoline	60 C	C
Hexane	60 C	B
Hydrochloric Acid, 30%	60 C	B,E
Hydrochloric Acid, 20%	60 C	A
Hydrogen Peroxide	60 C	B
Iodine Tincture	20 C	A
Ketones	20 C	A
Linseed Oil	60 C	A
Lubricating Oil/Motor Oil	60 C	B
Nitric Acid, 70%	20 C	C,E
Nitric Acid, 10%	100 C	A
Paraffin	60 C	B
Petroleum Ether	20 C	C
Phenol	60 C	A
Plating Solutions	60 C	A
Pyridine	20 C	A
Silicone Oil	60 C	A
Sugars and Syrups	60 C	A
Sulfamic Acid	60 C	A
Sulfuric Acid, 98%	20 C	C
Sulfuric Acid, 50%	60 C	B
Sulfuric Acid, 10%	100 C	A
Toluene	20 C	C
Trichloroethylene	20 C	C
Turpentine	20 C	C
Whisky	100 C	A
Wine	60 C	A

Code: A—Negligible Effect
 B—Limited Absorption or Attack
 C—Extensive Absorption or Permeation
 D—Extensive Attack
 E—May Produce Cracking Under Stress

Chemical Resistance of Mylar[®]

Substance	Conditions	Percent Retained (typical)		
		Tensile Strength	Elongation	Tear Strength
Acids				
Glacial Acetic Acid	24 hours, 75°C	100	100	100
Hydrochloric Acid, 10%		100	100	75
Hydrochloric Acid, Con.		0	0	0
Hydrofluoric Acid, 48%		80	50	50
Nitric Acid, 10%		100	100	100
Nitric Acid, 40%		0	0	0
Sulfuric Acid, 30%		100	100	100
Bases				
Ammonium				
Hydroxide, 2%	24 hours, 75°C	85	65	40
Sodium Hydroxide, 2%		90	65	40
Sodium Hydroxide, 10%		0	0	0
Solvents				
Dioxane (1,4)				
	24 hours, 75°C	100	100	100
Ethyl Acetate		100	100	100
Ethanol		100	100	100
Methyl Ethyl Ketone		100	100	100
Toluene		100	100	100
Trichloroethylene		100	100	100
Miscellaneous				
Detergent, 25%				
	24 hours, 75°C	100	100	125
Dimethyl Formamide		100	100	.
Sodium Sulfide, 4%		72	45	40
Tricresyl Phosphate		100	100	.
Impregnants				
Hydrocarbon oil, hi. vis.				
	900 hours, 100°C	92	88	87
Hydrocarbon oil, low vis.				
	(immersion)	98	67	123
Silicone, DC 200		79	141	97
Varnishes				
Asphalt Base GE9468				
	168 hours, 150°C	92	18	113
Glyptal Resin GE2480				
	(baked)	90	80	60
Phenolic Resin GE1678		92	3	73
Silicone Resin GESR80		58	230	100
Silicone Resin GESR28		100	54	97

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Chemical Resistance of Polycarbonate

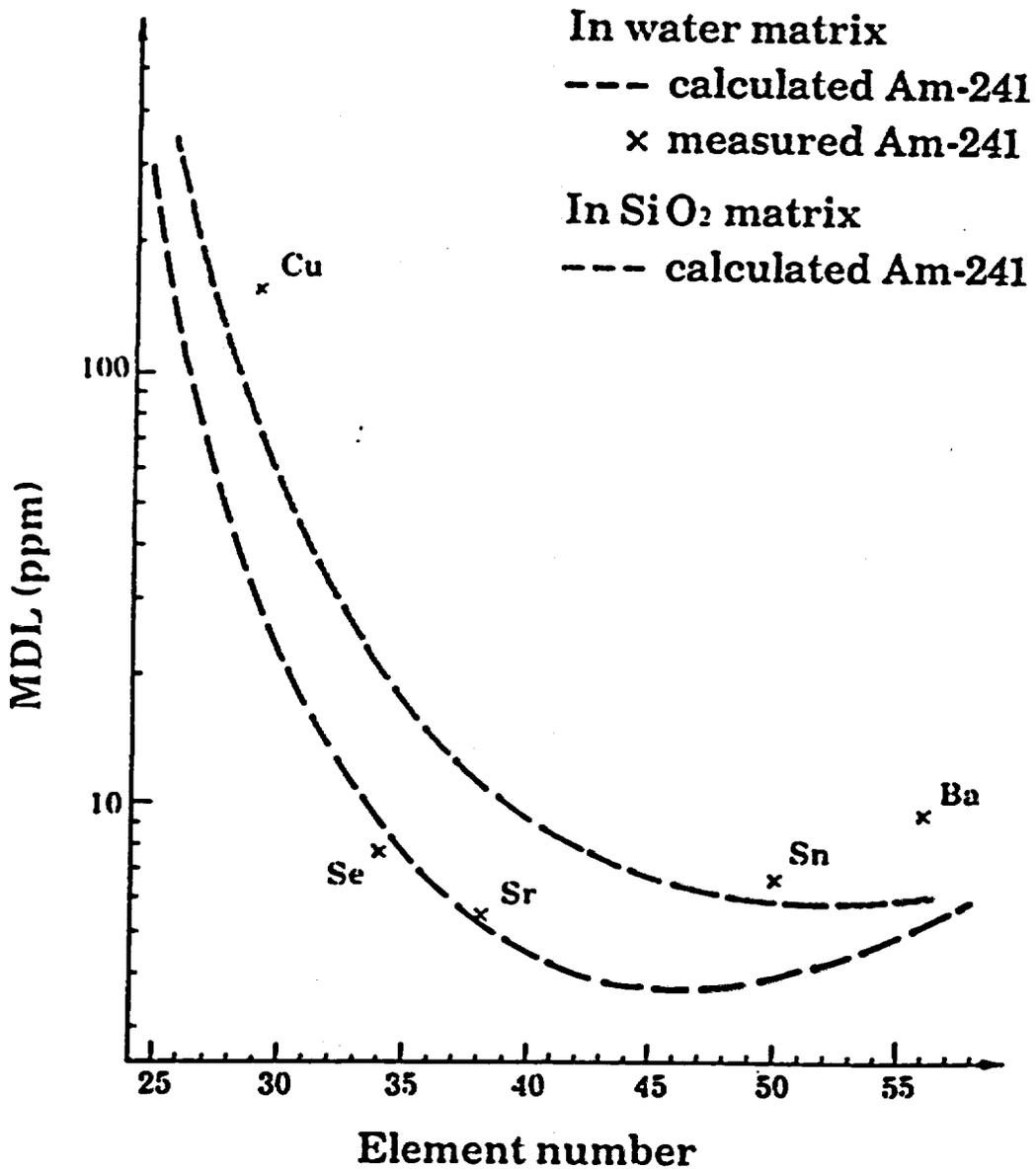
Substance	Conditions	Effect
Acetic Acid, 5%	30 days, R.T.	N
Citric Acid, 5%	6 days, R.T.	N
Cod Liver Oil	6 days, R.T.	N
Detergent Solution, 2%	30 days, R.T.	N
Freon 22	30 days, R.T.	P
Hydrogen Peroxide, 30%	30 days, R.T.	N
Iodine, Tincture	6 days, R.T.	N
Isopropanol, 70%	6 days, R.T.	N
Kerosene	6 days, R.T.	N
Lemon Juice	6 days, R.T.	N
Light Lube Oil	6 days, 80 C	N
Methyl Salicylate	6 days, R.T.	S
Oleic Acid	6 days, 80 C	N
Ozone, 1%	30 days, R.T.	C
Pine Oil	6 days, R.T.	N
Salt Solution, 10%	30 days, R.T.	N
Sardine Oil	6 days, 80 C	N
Shortening	6 days, 80 C	N
Soap Solution, 5%	6 days, R.T.	N
Soya Oil	6 days, 80 C	N
Wine	6 days, R.T.	N
Whiskey	6 days, R.T.	N

Code: N—No Effect
 S—Soluble
 P—Partially Soluble
 C—Chemically Attacked

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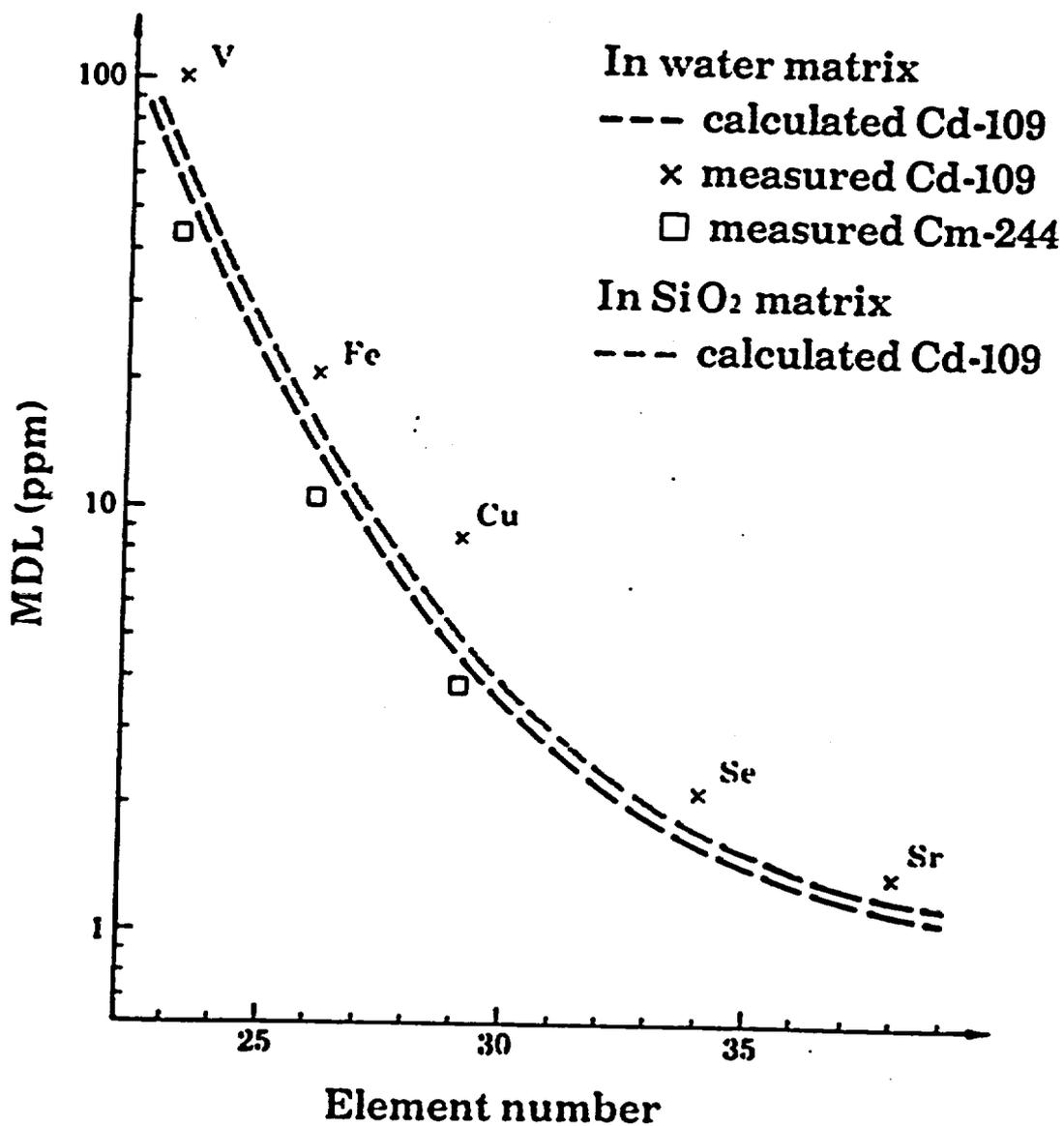
NOTE: Polycarbonate may be attacked by strong acids, bases, oxidizing agents, esters, ketones, aromatic and halogenated hydrocarbons.

Minimum detectable limits (3σ) for a measurement time of 4 minutes



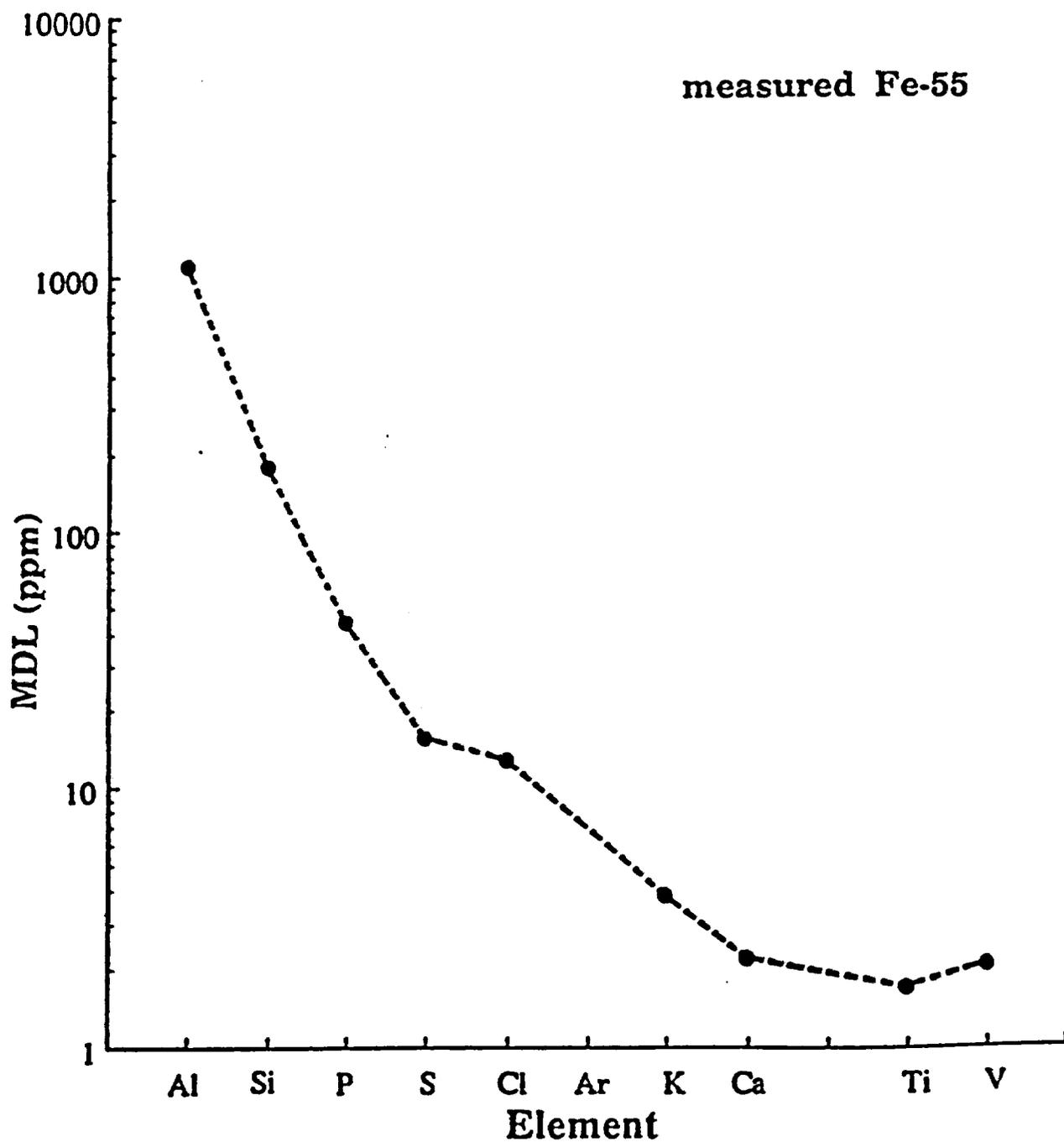
Metorex

Minimum detectable limits (3σ) for a measurement time of 4 minutes



metorex

Minimum detectable limits (3σ) for a measurement time of 10 minutes in water solutions, 50 μm Be window



Metorex

USING COMMUNICATION (TERMINAL) PROGRAMS WITH THE X-MET

- Select X-MET baud rate to 9600 using command CSI.
- Communication program:

Line Setup:

Baud Rate to 9600 (4800, 2400, etc...)
No Parity, 8 Data Bits, 1 Stop Bit

Terminal Options:

Terminal Emulation VT102 (VT100, VT52,...)
Full Duplex, XON/XOFF
No Hardware Flow Control
CR Translation CR

ASCII Transfer Options:

Character Pacing 0
Line Pacing 0.5 sec.
CR Translation (Upload/Send) NONE (or CR)
LF Translation (Upload/Send) STRIP (= Nothing is send)
CR Translation (Download/Receive) NONE
LF Translation (Download/Receive) NONE

HOW TO USE THE COMMANDS IPM/OPN, DMP/LOD

X-MET 880 Version 2.0 & X-MET 820 Version 4.0

Here CONT/YES = <CR> = <RETURN>
END/NO = <ESC>

Use CONT/YES to select an item, END/NO to move to the next, and ▲ to move to the previous item. If there are numbers between brackets, you are expected to select the appropriate one. “^D” is character for EOT (*End of Transmission*).

I. IPM/OPM (*Input/Output of Parameters*)

All the parameters can be uploaded and downloaded. The old interactive communication (*e.g. CIN, ASY*) of course can be used, but there is also a quicker way to move data: OPM/IPM. Both OPM and IPM are maintenance commands (*EMP must precede them*).

> OPM (Output Parameters)
MODEL (1-32) ?
PROBE (1-6) ?
CIN TABLE ?
ASY TABLE ?
LATEST SPECTRUM ?
PURE SPECTRUM ?
GAIN SPECTRUM ?
>

- The MODEL (*1-32*) corresponds to data under the PRM command, except that possible references (*REF*) are included.
- PROBE (*1-6*) corresponds to PRP.
- CIN TABLE corresponds to CIN.
- ASY TABLE corresponds to ASY.
- LATEST/PURE/GAIN SPECTRUM correspond to respective spectra of the SPL Command.

All communication takes place rapidly, one parameter per line, without text. The real numbers are moved in scientific exponential mode with seven (7) significant digits: *n.dddddE+e*.

EXAMPLES:

1. How to transfer (*download*) calibration intensities from the X-MET to the PC?

```

> EMP
> OPM
MODEL (1-32) ?   END/NO
PROBE (1-6) ?   END/NO
CIN TABLE ?    CONT/YES
Open input file and press <CONT>
(*) OPM calibration intensities (This is a header to the file in the PC)
:   (data)
:
^DCLOSE file and press <CONT> (**)
>

```

- (*) You must open a file on the PC by using a communication program (*download/ASCII in PROCOMM+*) and then press CONT/YES on the X-MET.

Result: Parameters are copied from the X-MET to the file on the PC.

- (**) The first character on that line is an end-of-transmission character. Close the file you opened by using the PC Program, and press CONT/YES.

NOTE: The data in the X-MET is not deleted.

2. How to transfer (*upload*) calibration intensities from the PC to the X-MET?

```

> IPM
MODEL (1-32) ?
PROBE (1-6) ?
CIN TABLE ?
Loading from PC (*)

OPM calibration intensities (header of file)
30 (data)
:
:
Close file and press <CONT> (**)
0 errors
>

```

- (*) You must send a file using PC's communication program (*upload/ASCII in PROCOMM+*).
- (**) This comes from the uploaded file; see Example 1 last line: the same line goes into the PC, and comes out during the uploading of the file, but the X-MET ignores this message. It is not necessary to do anything.

NOTE: If the pure element calibration in the X-MET is different compared with the loaded file, there will be a **WARNING: CHECK CHANNELS!** Transferred calibration intensities are however accepted. Data should not be used to create a model before correcting the setting of pure element channels (*deleting those not in use - adding missing ones*).

INPUT BUFFERING IN IPM

Model Parameters:

If no errors occur when transferring model parameter, parameters are saved in the X-MET.

If there are also references in an identification model (*X-MET 880*), the references are transferred so every reference which is transferred free of error is saved, and other references are not accepted.

Other parameter areas are fully buffered that is if there are errors and nothing is changed in the X-MET.

II. **DMP/LOD (*Dump Model Parameters/Load*)**

There is an additional feature for maintenance purposes:

Everything in the MMU memory between two addresses can be uploaded and downloaded in the hexadecimal ASCII format, or as the Motorola S-records (*contains also the address and check sum of each line*). The hexadecimal output can be long (*contains also the address of the line, and the conversion to ASCII characters*) or short (*only contents*), 16 memory bytes per line.

Also, you can use symbolic names for some parameter areas:

> DMP
S-RECORDS ?
WHOLE MEMORY ?
MODEL (1-32) ?
IDENT. LIBRARY ?
CALIBRATION TABLE ?
GAIN PARAMETERS ?
LATEST SPECTRA ?
PURE SPECTRA ?
GAIN SPECTRUM ?
GIVE THE FIRST ADDRESS :

WHOLE MEMORY is possible only in the S-record format. This can be used for backing up the X-MET memory; transferring takes about 20...30 minutes.

MODEL (1-3) contains one model selected by the user.

IDENT. LIBRARY contains all references of all models.

CALIBRATION TABLE contains data of both CIN and ASY.

GAIN PARAMETERS contains all parameters of all probes.

LATEST SPECTRA contains all three of the latest spectra.

PURE SPECTRA contains all the pure element spectra.

GAIN SPECTRUM contains the latest gain control spectrum.

Give the First (*Last*) Address: Data area to be dumped can also be given by addresses.

EXAMPLES: (*See examples in IMP/OPM too!*)

```

> DMP
S-RECORDS ?           CONT/YES
WHOLE MEMORY ?       END/NO
MODEL (1-32) ?      END/NO
IDENT. LIBRARY?     END/NO
CALIBRATION TABLE ? END/NO
GAIN PARAMETERS ?   CONT/YES
Open input file and press <CONT> (*)
SONN GAIN PARAMETERS
S21401EBC600480055003A00473FA9DBBC854ABACB48
S21401EBD6407F894CFE73916900B3002840B77000E8
:
:
S20C01ECF600000000000000000010
S8
^DClose file and press <CONT> (**)
>

```

NOTE: S0 = Header; S2 = Data; S8 = End

(*) You must open a file on the PC using PC's communication program (*download: ASCII in PROCOMM-*) and then press CONT/YES on the X-MET.

Result: Parameters are copied from the X-MET to the file on the PC.

(**) See Example 2 in IPM/OPM.

1. Dumping gain control parameters in hexadecimal ASCII long form (*Cannot be Uploaded to the X-MET*):

```

> DMP
S-RECORDS ?           END/NO
MODEL (1-32) ?      END/NO
INDENT. LIBRARY ?   END/NO
CALIBRATION TABLE ? END/NO
GAIN PARAMETERS ?   CONT/YES
FULL DISPLAY ?      CONT/YES
01EBC6:    00 48 00 55 00 3A 00 47 3F A9 DB BC 85 4A BA CB.H.U.:G?....J
:
:
01ECF6:    00 00 00 00 00 00 00 00 .....

```

2. Dumping gain control parameters in hexadecimal ASCII short form (*can be loaded back to the X-MET, if address is known*).

```

> DMP
S-RECORDS ?           END/NO
MODEL (1-32) ?       END/NO
IDENT. LIBRARY ?     END/NO
CALIBRATION TABLE ? END/NO
GAIN PARAMETERS ?   CONT/YES
FULL DISPLAY ?      CONT/YES
Open input file and press <CONT> (*)
00480055003A00473FA9DBBC854ABACB
407F894CFE73916900B3002840B77000
:
:
0000000000000000
^DClose file and press <CONT> (**)
>

```

- (*) You must open a file on the PC using PC's communication program (*download/ASCII in PROCOMM+*) and then press CONT/YES on the X-MET.

Result: Parameters are copied from the X-MET to the file on the PC.

- (**) See Example 2 in IPM/OPM.

3. Uploading gain parameters from the PC to the X-MET as Motorola S-Records (*transfers always to correct address*).

```

> LOD
S-RECORDS      CONT/YES
Loading from PC (*)

SONN GAIN PARAMETERS
S241401EBC600690072005F00683F8B49DC48FC45E03F
:
:
S8
0 errors
>

```

(*) File must be sent from the PC program with the upload.

4. Uploading gain parameters in hexadecimal ASCII short form from the PC file (*only the length of the data is checked*).

```

> LOD
S-RECORDS          END/NO
MODEL (1-32) ?    END/NO
IDENT. LIBRARY ?  END/NO
CALIBRATION TABLE ? END/NO
GAIN PARAMETERS ? CONT/YES
01EBC6 (*)
01EBC6:00690072005F00683F8B49DC48FC45E0
01EBD6:406E36E56B68EFD50080002840B77000
:
:
0 errors
>

```

(*) Address to where data is uploaded. File must be sent from the PC program with up/download.

INPUT BUFFERING IN LOD

One line at a time is buffered, and if the line is faultless the data on the line is saved.

NOTE 1: The S-Records are transferred to the same places in the X-MET memory, because they have the addresses with them. The hexadecimal short records can be moved anywhere, so it is not advisable to use this option, if one is not familiar with the Motorola 68000 Processor.

NOTE 2: When symbolic parameter area names (*e.g. gain parameters*) are used, the length of the area is checked and in case of errors a message will be displayed. In practice this means that wrong data can be transferred, if of appropriate length and must be replaced with proper data.

NOTE 3: The LOD command accepts consecutive bytes starting from a given address to be uploaded to the X-MET. The addresses can be given manually (*as command ICUMMU*) or uploaded from a PC file.

DATA INSIDE OPM-FILES

These are examples of the data contents in OPM-files. Texts after a colon are comments, which does not belong to the real files.

NOTE: After a header, there is a code number which is checked by IPM.

Model parameters (*MODEL (1-32) ?*):

The OPM data is basically the same as under the PRM (*Model Parameters*) command:

OPM Model 10 Parameters	: header
1	: code for IPM
10	: measuring time
NI-IDENTIFICATIO	: model name
IDENT	: model type
8	: pure element channels in model
0	: flow check channel
0.000000e+00	: channel intensity limit
6000	: max count rate
1.000000e+02	: safety percent
270991	: date of model
1.000000e+00	: B/A source meas.time ratio
1	: channel number
TI	: channel element
2	: probe number
B	: source of probe (A/B)
84	: channel low limit
101	: channel high limit
93	: peak channel
1.000000e+00	: normalization coefficient
1.000000e+00	: original coefficient
-2.556134e+01	: safety low lim. (Low calibr.int.)
-1.210501e+01	: safety high lim. (High calibr.int.)
2	: channel n:o (channels 2-10 are as channel 1)
CR	
2	
B	
105	

118

116

1.000000e-00

1.000000e-00

-9.722575e+01

9.361846e+02

1.043987e+00 : g-matrix starts here and is lited line by line

-2.133729e-01 : ted line by line

0.000000e-00

0.000000e-00

0.000000e-00

0.000000e-00

0.000000e-00

1.187308e-01

0.000000e-00

0.000000e+00

-2.216187e-01

2.10832e-00

0.000000e-00

0.000000e-00

0.000000e+00

0.000000e+00

0.000000e+00

-1.731373e+00

0.000000e+00

0.000000e-00

0.000000e+00

0.000000e+00

1.046341e+01

-1.008790e-01

2.365445e-02

-5.243575e-02

-2.380786e-02

0.000000e+00
 0.000000e+00
 0.000000e+00
 0.000000e+00
 -2.039909e-01
 etc...

NOTE: Only the intensities of the measured pure element channels (*) of the references will be transferred.

14 : number of references in the model
 1.103000e+01 : fine threshold
 7.39000e-01 : coarse threshold
 0.000000e+00 : channels 1-10 relative ranges
 0.000000e+00
 0.000000e+00
 0.000000e-00
 0.000000e+00
 0.000000e+00
 0.000000e+00
 0.000000e+00
 0.000000e+00
 NO : test value toggle YES:NO of ID test value
 14 : number of references in model
 8 : number of channels in model (*)
 ST : name of 1st reference
 100 : measuring time of reference
 -1.890179e+01 : intensities of reference pure element
 9.361846e+02 : channels
 2.012996e+02
 6.829490e+02
 6.028700e+01
 5.462162e+00

3.551000e+02

1.919600e+03

COGWHEEL-ST : name of 2nd reference

100

-1.210501e+01

-5.357485e+00

6.891531e+00

4.464652e+01

-2.038903e+02

2.352436e+03

3.384000e+ 02

1.43000e+03

1SEK : name of 3rd reference

100

^D Close File and press <CONT> : This is the last line of the file

: The first character ^D is EOT (*end of transmission*) comes from the X-MET

: = (ASCII 4)

If the model type is ASSAY then the file is different after the G-matrix:

: G-matrix ends
 2 : number of dependents
 CU : 1st analyte (*dependent*)
 FE : 2nd analyte (*dependent*)
 : empty lines n...6, when no more analytes
 2 : number of indeps for the 1st analyte
 1 : number of indeps for the 2nd analyte
 0 etc...
 0
 0
 0
 CU*FE : 1st analyte independents, lists one after the other
 BS2

: empty lines x...6 when no more indeps.

	: empty lines x...6 when no more indeps.
	:
FE	: 2nd analyte indeps etc...
	: empty lines y...6 when no more indeps.
	: empty lines for ...6 analytes
-7.941022e+01	: Coefficients are listed starting from 1st
1.666205e-02	: analyte intercept, then slopes for indeps
2.151726e-01	
0.000000e+00	
0.000000e+00	
0.000000e+00	
0.000000e+00	
2.360086e+00	etc...
STAND 14/2	: name of standard sample
150	: measuring time of standard
0.000000e+00	: 1st analyte original assay (<i>standard</i>)
0.000000e+00	: 2nd analyte (1st...6th) etc...
0.000000e+00	
0.000000e+00	
0.000000e+00	
0.000000e+00	
0.000000e+00	: 1st analyte original intercept
0.000000e+00	: 2nd analyte (1st...6th) (<i>standard</i>)
0.000000e+00	
0.000000e+00	
0.000000e+00	
0.000000e+00	
^D Close file and press <CONT>	: end of file, close file on PC

If the model type is UNDEF, then after G-matrix there are only a few lines:

Calibration unfinished

^D Close file and press <CONT>

PROBE PARAMETERS (PROBE (1-6) ?)

The probe parameters are the same as under command EMP/PRP, see the X-MET manual.

OPM probe 2 parameters	: header
2	: code for IPM
92	: a low
102	: a high
81	: b low
91	: b high
5.937567e-02	: t0
3.102593e+02	: slope
128	: gain
INI	: mode (INITNG)
6.000000e+03	: frequency limit
6	: probe type (6=DOPS)
BS	: reference limit
CD	: source A
FE	: source B
0.000000e+00	: resolution (not set if 0)
270991	: date of initialization

CALIBRATION ASSAYS (ASY TABLE ?)

Calibration assays are the reference assays fed in with command ASY.

OPM calibration assays	: header
4	: code for IPM
4	: number of calibration samples
2	: number of dependents
CU	: 1st analyte
FE	: 2nd analyte
1.56000e-01	: 1. Sample 1. Analyte conc. (Cu)
6.023000e+01	: then 2. Analyte conc. (Fe)
3.62000e+01	: 2. Sample 1. Analyte conc. (Cu) etc...
9.20000e+00	

3.62000e+01 : 2. Sample 1. Analyte conc. (Cu) etc...
 1.02000e+01
 1.250000e-02
 1.295600e+01
 2.142000e+00
 ^DClose file and press <CONT>

SPECTRUM OUTPUT (LATEST SPECTRUM?)

OPM latest spectrum PR2 : header
 5 : code for IPM
 2 : probe number
 A : source
 6 : probe type
 100 : measuring time
 2700991 : date
 17 : counts for channel 0
 0 : counts for channel 1
 .
 .
 3262 : counts for channel 255

^DClose file and press <CONT>

GAIN SPECTRUM (GAIN SPECTRUM?)

Open input file and press <CONT>

OPM gain spectrum PR3 : header
 7 : code for IPM
 3 : probe number
 A : source
 1 : probe type
 60 : measuring time
 270991 : date
 5 : counts for channels 0 to 255
 .
 .

S

: counts for channels 0 to 255

11782

: counts in channel 255

*DClose file and press <CONT>

Metorex

SOFTWARE GUIDE
X-MET 880 / VERSION 2.0
(CHANGES TO VERSION 1.0.1)
3885-399-4VE

SKVEK 26.9.1991

SOFTWARE GUIDE FOR X-MET 880 VERSION 2.0

I. NEW FEATURES

1. IMPROVED AUTO SCREENING

Working with the DOPS probe.

New Feature:

Possibility to stop/continue screening, for instance from sorting model to an assay model, by naming the reference in two parts, for instance: SS237.AS237. The screening stops at SS237 and can be continued by <Cont>, whereby model AS237 is reached or screening can be terminated by <(Backspace)>.

Bug of Version 1.09.1 Corrected:

Program did not check the probe when jumping to another model; version 2.0 will deliver a message: MAKE NEW MEASUREMENT, if the probe is not the same.

2. CLOCK NORMALIZATION

The source decay compensation is made automatically based on the real time clock. The procedure changes the values of the normalization coefficients likewise the manual normalization does.

During performing the 'INI' command the user is asked to define the sources the probes contain. Possible notations are Am, Cm, Cd, Fe, Pu. The normalization coefficients are then updated once a day, or if the X-MET has been left with the power on for the night, at 24.00 hours. The message: CALCULATING NORMALIZATION COEFFICIENTS is displayed during calculations.

When a pure element calibration is made (PUR), the date is stored as a model parameter (can be displayed by PRM). The normalization formula is $n = n_0 \cdot \exp(-\ln 2/T \cdot dt)$ where:

- n = New Normalization Coefficient
- n₀ = Former Normalization Coefficient (originally set to 1 by 'PUR')
- T = Half-life of the Source
- dt = Time Interval between Present and 'PUR' Time

Also, n₀ can be manually adjusted by "PRM", and the effect can be immediately seen by making the normalization using command "CNF" (Calculate Normalization Factors).

If the date has not been given, "PUR" does not proceed. Instead a message: SET DATE AND TIME first appears. If the date has been lost, no updating of normalization parameters is made until "STM".

3. PARAMETER UP/DOWNLOAD

All the parameters can be up and downloaded in ASCII format by using commands "OPM" (*Output Parameters*) and "IPM" (*Input parameters*).

For maintenance purposes two additional commands are provided: "DMP" (*DUMP*) and "LOD" (*LOAD*). Everything in the XMMU memory between two selectable addresses can be up/downloaded in hexadecimal ASCII format or as Motorola S-records (*also contains the address and check sum of each line*). These commands can also be used for parameter areas without knowing the memory addresses.

4. PROBE RESOLUTION CHECK-UP

The probe resolution R is calculated as follows:

$$R = F * \text{sqrt}(E/5.9) \quad \text{where} \quad R = \text{Apparent Resolution given in Percents}$$

$$F = 100 * (\text{FWHM/Peak Channel}), \text{FWHM in Percents}$$

$$E = \text{Energy of the Reference Line in keV}$$

NOTE: The probe resolution value is always about 2% units worse than the certified resolution of the counter tube.

The initial resolution R of a probe is measured by the maintenance command "IRS":

```
> EMP
> IRS
PROBE 3: REFERENCE FE ? CU <Cont>
MEASURING PROBE 3 TYPE HEPS
60 SECONDS
RESOLUTION 18.3%
>
```

Possible references are: Cu, Mo, Ti, W. The resolution is stored in the probe parameter memory and can be displayed by "PRP".

Later on, the change of resolution can be checked by using "RES":

```
> RES
MEASURING PROBE 3 TYPE HEPS
60 SECONDS
RELATIVE RESOLUTION: 1.012
```

NOTE: "RES" outputs a relative resolution value (*calculated/initial*). This resolution ratio is displayed also during the gain test procedure ("GTS").

If the reference element is not defined (*or differs from the list above*), only the FWHM % is calculated.

5. SAFETY LIMITS FOR THE USE OF A MODEL

During the "MOD" procedure for each element, the maximum and minimum values of the intensities encountered among the calibration samples are automatically recorded in the memory. If during a measurement, the calculated intensity of any channel exceeds its record limits by p %, where p is a model dependent parameter, a message is displayed:

**CALIBRATION LIMITS EXCEEDED:
> FE CU NI ZN**

NOTE: The user can override this message and get the final assays by using <Recalc> command.

II. IMPROVED PROCEDURES

1. DOPS OPERATION

Bugs in Version 1.0.1. Now Corrected:

- "TSM" measures the sample using source A, too.
- If during a "PUR" sequence a measurement with source A is interrupted, the program asks ... TRY AGAIN? If the answer is <Autostart>, the new measurement done with source A is also taken properly as A measurement (*not B as erroneously earlier*).
- Answering <Yes> from terminal to the following questions does not anymore erroneously change the source:

**COUNT RATE TOO HIGH
CONTINUE?**

and

**MEASUREMENT INTERRUPTED
TRY AGAIN?**

- The latest spectrum from both sources is saved. Now also "TCR" gives total rates of both sources. Likewise <Recalc> now reacts correctly to dual source models.

Improvements

- Source time ration (*B/A ratio*) is model dependent (*not probe dependent*). It is asked in the beginning of the commands "ADD", "CAL", "AAC", if DOPS is used.
- The source is check in the beginning and in the end of the measurement. If some odd combination of trigger and XEDS signaling start a measurement with a wrong source, the resulting spectrum is ignored.

- When DOPS is connected to XEDS with other probes, the most convenient way to start a DOPS measurement is to use the <Start> key.

If at this time the gain control is running for another probe, it is interrupted and DOPS is switched on line. This results as a "TRY AGAIN?" question. Now the measurement can be started by the trigger.

2. IDENTIFICATION ANOMALIES RECTIFIED

- Multi-probe models have scaled the results by the sum of counts from all probes. Now each probe is processed separately.
- If an identification model is calibrated in conjunction of an assay model following erroneous behavior have been found possible:

> MDE (*Model m, Current Measuring Time = tm*)
 > CAL (*Measuring with Measuring Time = tm*)
 > MDE (*Switch to Model n, Measuring Time = tn*)
 > ADD <Recalc> (*Recalculation with tn, should be = tm*)
 > CAL

When t_n differs greatly from t_m , the results may be erroneous. To avoid this, use same measuring times for both models.

NOTE: This happens only when measurements are made in "CAL" and then recalculated in "ADD". If the measurements are done in "ADD" or "AAC" everything works fine.

- "POSSIBLE MATCH" now displays as much of identification names as will fit on the display screen.

3. DISPLAY MESSAGES MORE INFORMATIVE

Some explanatory text has been added to measurement displaying screens.

- Following display is shown in connection to <Start>, "PUR", "CAL", "AMS", "FPI", "CMS", and "CMG":

MEASURING: PROBE 1 TYPE HEPS 15s
 15 SECONDS LEFT SH 10

- Following applies to "MST", "STA":

MEASURING: PROBE 1 TYPE HEPS 15s
 STANDARD 15 SECONDS LEFT SH 10

- Following results from "INI":

MEASURING: PROBE 1 TYPE HEPS 15s
INITIALIZATION 60 SECONDS LEFT SH 32

- Following results from "TSM":

MEASURING: PROBE 1 TYPE HEPS 15s
SAMPLE TEST 15 SECONDS LEFT SH 32

MEASURING: PROBE 1 TYPE HEPS 15s
REFERENCE TEST 15 SECONDS LEFT SH 32

- Following results from "CHT":

MEASURING: 15s
CHANNEL TEST 10 SECONDS LEFT SH 32

Measurement prompts now contains the probe identifier, too:

MEASURE PR3 (and) MEASUREMENT INTERRUPTED
TRY AGAIN (PR3) ?

4. **KEYBOARD BUFFERING IMPROVED**

Key strokes entered when the analyzer is busy are stored and executed after the instrument has finished previous tasks. Version 1.0.1 waited erroneously an additional key stroke to activate the buffer.

5. **MORE MEMORY TO STORE SPECTRA**

The analyzer now can store up to four complete spectra: the last complete gain control spectrum and up to three spectra from latest measurement.

NOTE: The measured spectra are all from the latest measurement. The number depends of the number of sources involved in that measurement. The gain spectrum can be show only in "EMP state and it si always the last full 60 s spectrum.

The measured spectra may be also from multi-probe models, from DOPS measurement, etc... If the measurement was interrupted, this spectrum (*spectra*) can still be viewed by "SPE" and "SPL". The corresponding header only bears text "STOPPED" instead of "MEAS.TIME".

6. GAIN CONTROL PROCEDURE IMPROVED

Now the gain control includes only one basic measurement. The spectrum is recorded in 60 s periods. The slope is now determined during the probe initialization process mathematically.

As before shorter than 60 s (*interrupted*) periods are taken into account whenever they are statistically meaningful.

During the first minute after power-up the gain control is not active. This also prevents unnecessary "COUNT RATE TOO LOW" messages during this period.

The gain control procedure now continues also after "TOO BIG GAIN CHANGE" and "GAIN OUT OF RANGE" messages.

The use of the manual distributor box for multi-probe applications is now easier to use. When the probe is changed, the X-MET automatically searches for the right probe number. If it is not found or is ambiguous, the gain control is not performed until a valid probe is found.

7. AUTOSTART FOR MULTI-PROBE MODEL

This feature works only with XEDS.

During a measurement the XEDS steps through its six positions to meet all the probes belonging to the present model. The first probe is always the probe on first position. If the second (*third ... nth*) probe in the model is ready, the measurement with it starts immediately. If not, a message is shown: MEASURE AGAIN WITH PROBE N. When command "ADD", "AMS", "CAL", "FPI", "MST", or "STA" is applied to XEDS multi-probe model, the first probe is always identified in "MEASURE..." message.

8. MEASURING TIME SETTING POSSIBILITIES EXTENDED

Measuring time can be changed at the beginning of commands "ADD", "AAC", "CAL", "PUR", and "MST".

9. B/A RATIO SETTING FOR 2 PROBE MODELS

If a model contains a DOPS probe, the B/A ratio setting option is reserved for that.

If a model is based on the utilization of two single source probes, the B/A ratio determines the measurement time of the second probe. The measurement time of the first probe is given in a normal way.

10. BATTERY LOW SIGNAL UPDATED MORE FREQUENTLY

The charge status of the battery is checked now at least once a minute when nothing else is done (*at prompt*), and every time the XMMU is called or put in sleep.

11. ANALOG OUTPUT RANGE

Analog output range is now -32768...+32767 instead of 0...255 in the previous software versions.

III. CHANGES IN OTHER COMMANDS

1. AAC (NEW COMMAND)

This command combines "ADD" and "CAL" enabling flexible building of assay and identification models based on the same calibration data.

Example:

```
> ACC
MEASURING TIME 15 ? 60
IDENT. MODEL ? 28
LIBRARY: AAC TEST ID      O REFS.
ASSAY MODEL ? 29
NO OLD DATA
1. REF: NAME? SAMPLE 1
MEASURE
MEASURING: PROBE 5 TYPE HEPS
2 SECONDS
2. REF: NAME? <End>
    1 REFS. AND 1 SAMPLES
```

(New Model)

```
> ACC
MEASURING TIME 2 ?
IDENT. MODEL ? 28
LIBRARY: AAC TEST ID      1 REFS.
ASSAY MODEL ? 29
OLD DATA: 1 SAMPLES
2. REF: NAME? SAMPLE 2
MEASURE
MEASURING: PROBE 5 TYPE HEPS
2 SECONDS
3. REF: NAME? <End>
    2 REFS. AND 2 SAMPLES
```

(Old Model)

2. AMS

Immediate termination of "AMS" procedure no more results as an "INTEGER OVERFLOW" message.

Calculates now also the standard deviation of the set of measurements.

3. CMS/CMG

A header is ended now with a single <End>.

If no probes are found connected, gives an error message.

No more probe check errors during initial gain control.

If the continuous measurement sequence has no model defined, the command is executed using current model. Then and only then, averages are also shown. The user can also make a preset number of measurements.

Example 1:

```
> CMS
HOW MANY MEASUREMENTS ? 2
ASSAYS ?
HEADER ? <Yes>
NO SEQUENCE DEFINED <End>
```

This produces following printout:

```

                                X-MET 880
*** CONTINUOUS MEASUREMENT: Concentrations ***
    DATE: 13.09.91          (MODEL 20: HEPS ASSAY)

Time      NI      CU      FE      W      MO
10-00-57  5.397  2.683  0.000  5.898  .023
AVERAGES: 5.397  2.683  0.000  5.898  .023

10-01-03  5.755  .141  0.000  5.405  .684
AVERAGES: 5.576  1.412  0.000  5.651  .354
```

Example 2:

> SEQ
 POSITION 1: MODEL 0 ? 20
 POSITION 2: MODEL 0 ?

> CMS
 HOW MANY MEASUREMENTS ? 2
 ASSAYS ?
 HEADER ? <Yes>
 SEQUENCE DEFINED <End>

This produces following printout:

X-MET 880
***** CONTINUOUS MEASUREMENT: Concentrations *****
DATE: 13.09.91

Time	MODEL	NI	CU	FE	W	MO
10-01-47	HEPS ASSAY	1.299	8.446	0.000	7.417	3.751
Time	MODEL	NI	CU	FE	W	MO
10-01-52	HEPS ASSAY	3.368	11.58	0.000	0.000	0.000

4. **CSI**

The number of baud rate choices is reduced: 110, 300, 1200, 2400, 4800, 9600, and 19200. When changing the baud rate, scrolling starts from the current value.

5. **DEL**

Deletion of pure element spectra is removed from command "PUR" and moved to "DEL":

> DEL
 WHICH MODEL TO DELETE (1-32) ? <No>
 DELETE PUR SPECTRA ? <Yes>
 ARE YOU SURE ? <Yes>
 PUR SPECTRA DELETED

6. **INI/ING**

If the probe already was initialized, a message is shown:

**PROBE ALREADY INITIALIZED (HEPS)
REINITIALIZE ?**

7. **LIM**

A warning of overlapping channel limits has been added:

WARNING! OVERLAPPING LIMITS

In spite of the message, the limit settings are accepted.

8. **MO1/MO2 (NEW COMMAND)**

MO1 = Change to Model 1 (*also measuring time*)

MO2 = Change to Model 2 (*also measuring time*)

These two commands can be programmed into function keys. This may be required, for example, when the keyboard is locked (*except F-keys*) and nevertheless a switch over is required between two models or model lines.

9. **MOD**

- There has been confusion in the residual numbering when sample points have been removed from calibration data. Now the numbering follows always calibration data. Now the numbering follows always the original tagging. Removing a sample point from the set does not affect to the identification numbers of the others.
- Removing sample points happens similarly to deleting points.

**DELETE POINTS: <No> OR <Cont>
RECOVER POINTS: 3 23 <Cont>**

R=0.990 S=0.838 F(2,17) =401.2

- Scaling of the residual plot spans now from the minimum value to the maximum value found among the data. Also, scaling axes are marked with three significant digits accuracy.

Negative intensities are now handled correctly in the plot.

- Leaving the "MOD" command cleans up the unused slope values from the independent parameter table. All unused parameter positions show up as 0s.

10. PAR

Checkpoints are added to eliminate input errors:

> PAR

OLD DEPENDENTS: CU FE CR NI

NEW ? P

NEW DEPENDENTS: p ? <No>

NEW ? <No>

CU-PARAMETERS (YES/NO) ? <Yes>

...

Coefficients:

INTERCEPTS: 2E+1 ? P (Correct "Print")

...

>

11. PRM

- New parameters:
 - PUR date
 - Initial Normalization Coefficients
 - B/A Ratio
 - Show Test Variable (*ON OFF Identification*)
- Removed Parameter:
 - Normalization Intensity
- Unused slope values or relative range values are no more printed.
- Minor changes in parameter tests and lay-out.

NOTE: All new parameter values must be explicitly types, i.e., a new value of a parameter must be given in a complete form.

12. PRP

- New parameters:
 - INI date
 - Source(s)
 - Frequency Limit (*Gain Control*)
- Removed Parameters:
 - S Count (*Not Used*)
 - Auto Normalization Parameters
 - B/A Ratio (*DOPS*)
 - Model (*Not Used*)

- None is an allowed probe type designation.

NOTE: All new parameter values must be explicitly types, i.e., a new value of a parameter must be given in a complete form.

13. PUR

- Pure element spectra deletion is moved to command "DEL".
- Added check-up against repeated input:

```

MODIFY ELEMENTS ? <Yes>
NEW MEASUREMENT CUI ? <No>
2. PURE ELEMENT: CU
CU ALREADY GIVEN           (Added Warning)

```

14. REF

The intensities of the reference of an identification model can be displayed and changed.

```

> REF
NAMES ? <Yes>
LIBRARY 7:...      13 REFS
... <End>
INTENSITIES ? <Yes>
13*3 INTENSITIES
1.REF TI2B: 393.627 ? <Cont>
1.REF CR2B:   301.662 ? <Cont>
1.REF BS2B:   98.1483 ? <Cont>
1.REF TI2B: 429.409 ? <Cont>

```

15. RST

A confirmation message added:

```

> RST
TOTAL RESET ? <Yes>           (or)
TOTAL RESET DONE
>
> RST
TOTAL RESET ? <No>
NOTHING CHANGED
>

```

16. RWM

Error recognition improved.

17. SPL/SPE

When selecting the last spectra for inspection or output, the choice are shown:

```
> SPL
LATEST SPECTRUM ? <Yes>
1: PR3      2: PR5A    3: PR5B
SELECT SPECTRUM:
...
```

18. STA

Standard correction is prevented until 30 minutes after power-up. If "STA" is tried before a message is shown:

NOT READY FOR STA MEASUREMENT

Also strongly deviating results are now possible to accept:

```
> STA
...
WRONG STANDARD ? <Yes>  (Really wrong)
```

(or)

```
>STA
...
WRONG STANDARD ? <No>  (accepted)
```

19. TCR

Shows all count rates of the latest non-interrupted measurement. If "EMP" is on, total count rate of latest full gain control spectrum is displayed:

```
> TCR
TOTAL COUNT RATES:
PR1: 2547  PR5A: 4537  PR5B: 2087
> EMP
> TCR
TOTAL COUNT RATES: 1234 (G)
PR1: 2547  PR5A: 4537  PR5B: 2087
```

20. TSM

Changed to a normal command set (from "EMP" set).

21. VER

XMMU/XICU version and date:

NOTE: Date is removed from power-up display.

APPENDIX 1: USER COMMANDS

***	Comment
AAC	Automatic Add/Cal with Same Samples
ADD	Addition of Reference Samples to the Library
AMS	Average Measurement calculation
ASY	Entry of Assays
BLT	Display Backlight On/Off
CAL	Measurement of Calibration Samples
CAO	Configuration of Analog Output
CHR	Send ASCII Character codes
CIN	Output of Calibration Sample Intensities
CMG	Continuous Measurement with Gain Control
CMS	Continuous Measurement
CNF	Calculate Normalization Coefficients Again
CSI	Configuration of Serial Interface
DEL	Delete Model/PUR Spectra
DTM	Display Date & Time
FNC	Function key Programming
FPI	Pass/Fail Identification output
FRQ	Set Check Count Rate
HLP	Help
ING	Initialize Probe from CMG
INI	Initialize Probe
INT	Output of Channel Intensities
LIM	Examine/Change Channel Limits
LOC	Locking of Keyboard
MDE	Choice of Model = <Model> = control-D
MOD	Regression modeling
MO1	Change to Model 1
MO2	Change to Model 2
MST	Initial Measurement of Standard Sample
MTM	Set Model Time
PAR	Examine/Change Regression Parameters
PUL	Output of Gross Count Rates of Channels
REC	Pure Element Calibration
REF	Recalculation = <Recalc> = Control-R
RES	Examination & Renaming of Reference Samples

...	Comment
SEQ	Check Resolution
SPE	Set Sequence for CMS/CMG
SPL	Output of Spectra
SPR	Spectrum Plot
SS2	Select Probe
STA	Select source B in DOPS/SSPS
STD	Standard Correction Measurement
STM	Set Date & Time
STR	Start Measurement = <Start> = control-A
TCR	Output of Total Pulse Count Rate
THD	Output of Default Identification Thresholds
THR	Examine/Change Identification Thresholds
TIM	Change Measurement Time = <M.Time> = Control-T
TSM	Test Measurement
VER	Show Program Version/Date
CHK	Soft Restart
CHT	Channel Test
DMP	Dump MMU Memory
EMP	Entry of Maintenance Commands
GTS	Test Gain Outputs
ICU	Examine/Change ICU-memory
IPM	Input Parameters
IRS	Initial Resolution
LOD	Load MMU Memory
MMU	Examine/change MMU Memory
OPM	Output parameters
PCT	Probe Control test
PRM	Examine/Change Model Parameters
PRP	Examine/Change Probe Parameters
RST	Total Reset
RWM	Read/Write Memory Test
TAO	Analog Output Test
TSI	Serial Interface Test
UNL	Unlocking of the Keyboard
XMP	Exit of Maintenance Commands

APPENDIX 2. EXAMPLE OF PRM

A. Assay Model

>prm
 MODEL 20 ?
 GENERAL PARAMETERS ? p

General parameters:

Name	Max c.rate	PUR date	Type	Meastime	Channels
HEPS ASSAY	6KHz	220891	ASSAY	2	4
Flow Channel, int.limit		Safety %	B/A ratio		
0	420.00	100.00	1.00		

Channel Parameters:

Chnl	EI	Pr	S	Low	High	Peak	Norm.coeff.	Orig.coeff.	Slow	Shign
1	NI	1	A	90	99	96	1.0182	1.000	100.4526	2190.9870
2	CR	1	A	64	75	70	1.0182	1.000	320.8767	1234.0984
3	FE	1	A	77	88	83	1.0182	1.000	298.9067	3092.1234
4	BS	1	A	255	255	255	1.0182	1.000	897.8767	2198.2234

G-matrix:

	1	2	3	4
1	1.276	.025	-.203	-.130
2	.019	1.018	-.118	-.092
3	-.168	-.145	1.051	-.132
4	.000	.000	.000	1.000

Assay parameters:

3 dependents:

Dependent	Name	No of Indep's
1	NI	1
2	CU	3
3	FE	2

Functions:

Dep	f1	f2	f3	f4	f5	f6
1	NI					
2	CU	NI*CU	CU/			
3	FE	FE/				

Coefficients:

Dep	Intercept	Slope1	Slope2	Slope3	Slope4	Slope5	Slope6
1	3.245	10.43					
2	-7.123	2.345	-0.987				
3	3.567	6.709					

Standard: ST3025 Meas.time: 15
 Dep Assay Original Intercept
 1 30.546 2.8900
 2 3.6530 -7.1234
 3 1.5674 3.5670

b. identification Model

>prm
 MODEL 2 ? 1
 GENERAL PARAMETERS ? p

General parameters:

Name	Max c.rate	PUR date	Type	Meastime	Channels
SORT	15KHz	220891	INDET	2	6
Flow Channel, int.limit		Safety %	B/A ratio		
0	0.00	100.00	1.00		

Channel Parameters:

Chnl	EI	Pr	S	Low	High	Peak	Norm.coeff.	Orig.coeff.	Slow	Shgn
1	TI	2	B	84	100	92	1.0185	1.000	29.3627	124.0402
2	CR	2	B	105	118	116	1.0185	1.000	67.9776	230.1523
3	CR	2	A	60	70	65	1.0182	1.000	11.53747	221.8687
4	FE	2	A	71	82	77	1.0182	1.000	14.3555	363.4000
5	BS	2	A	255	255	255	1.0182	1.000	1816.8000	2028.8000
6	BS	2	B	119	130	121	1.0085	1.000		

G-matrix:

	1	2	3	4	5	6
1	1.021	-.153	0.000	0.000	0.000	.073
2	-.187	2.052	0.000	0.000	0.000	-1.598
3	0.000	0.000	1.049	-.155	-.021	0.000
4	0.000	0.000	-.189	1.090	-.112	0.000
7	0.000	0.000	0.000	0.000	1.000	0.000
8	0.000	0.000	0.000	0.000	0.000	1.000

Ident parameters:

No. Ref.	Fine Threshold	Coarse Threshold							
2	11.03000	73.90000							
Ref. Range									
Ch1	Ch2	Ch3	Ch4	Ch5	Ch6	Ch7	Ch8	Ch9	Ch10
.500	.500	.5000	.500	0.000	0.000				

Show Test Variable : YES

APPENDIX 3: EXAMPLE OF PRP

>prp
 PROBE NUMBER: 3 ? I
 GAIN PARAMETERS ? p

Gain control parameters:

Probe	Alow	Ahigh	Blow	Bhigh	T0	Slope	Gain Mode	Freq lim
1	105	114	95	104	.03148	237.45	132	6KhZ

Probe parameters:

Probe	Type	Reference	Sources A, B	Resolution	INI date
1	HEPS	CU	CD BS	13.56	220891

GAIN PARAMETERS ?
 PROBE PARAMETERS ?