

Desktop X-ray Fluorescence Element Analyzer (MESA-500)

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Abstract

HORIBA has developed the MESA-500 energy dispersive X-ray fluorescence analyzer. This analyzer is capable of extremely easily and accurately analyzing the amount of elements contained in all types of samples (solids, powders, liquids, etc.) in a non-destructive manner and without the need to use standard samples. The MESA-500 is in an extremely compact design, and enables even anybody to easily obtain highly accurate analysis information such as X-ray spectra, automatic qualitative analysis, standard-less quantitative analysis, etc. This paper describes how highly-accurate quantitative analysis has been achieved by methods such as spectrum processing whereby the intensity of fluorescent X-rays is calculated from measured spectrum data, and matrix compensation using fundamental parameter method.



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1. Introduction

Up till now, in order to carry out highly accurate quantitative analysis using a X-ray fluorescence analyzer, dilution processing such as the Glass Bead Method*1 had to be used in order to lessen the influence of coexistent elements. This was disadvantageous in that this resulted in a drop in measurement intensity. In particular, energy dispersive X-ray fluorescence analyzers using semiconductor detectors have many features such as compactness and the capability to analyze elements at high speed. On the other hand, however, as X-rays having a wide energy range including scattering X-rays were detected at the same time, there was a limit to the intensity of the fluorescent X-rays that could be measured, and quantitative accuracy was slightly lower than that of wavelength dispersive X-ray fluorescence analyzers. Nevertheless, recently, correction of the influence of coexisting elements by the fundamental parameter method (FPM) has eliminated the need to pre-process samples, and the excellent features of energy dispersive X-ray fluorescence analyzers, that are capable of obtaining sufficient measurement intensity with even a small excitation X-ray source, can now be demonstrated.

At HORIBA, we have thoroughly developed and modified various element technologies such as X-ray tubes, detectors, high-voltage power supplies, high-speed pulse processing circuits, and calculation and processing for signal recovery. As a result, we have developed the energy dispersive X-ray fluorescence analyzer MESA-500 (see **Fig.1**) that is in an extremely compact design, and enables even anybody to easily obtain highly accurate measurement results.

*1 Glass Bead Method

A material pre-processing method where powder samples are heated and dissolved in a solution such as lithium borate in order to obtain uniform glass.

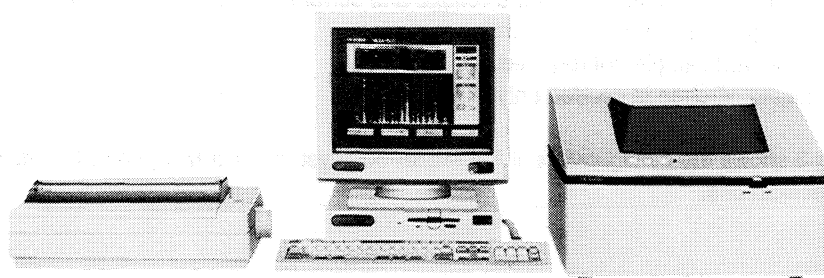


Fig.1 Energy dispersive X-ray fluorescence analyzer MESA-500

2. Energy Dispersive X-ray Fluorescence Analyzer MESA-500

As the energy dispersive X-ray fluorescence analyzer can separate X-ray energy at the detector itself, the distance between the sample and the detector can be reduced to be much shorter than that of a wavelength dispersive X-ray fluorescence analyzer that use a spectral crystals and a goniometer, and the detection solid angle can be increased. For this reason, this analyzer has various advantages: sufficient X-ray intensity can be obtained with a small excitation source, and the entire analyzer can be downsized. Also, the peak positions on the measurement spectra and intensity are hardly influenced even if there are slight changes in the evenness of the sample surface or the distance between the excitation source, sample, and detector. Accordingly, complicated pre-processing such as polishing or grinding of the sample are no longer required. Furthermore, the analyzing section of the MESA-500 has no moving parts such as a goniometer, as shown in **Fig.2**, which allows the analyzer to be constructed extremely simply and sturdily, and almost trouble-free. As a result of these features, energy dispersive X-ray fluorescence analyzers are quickly gaining in popularity in a wide range of applications not only in research laboratories but also in quality control and processing control.

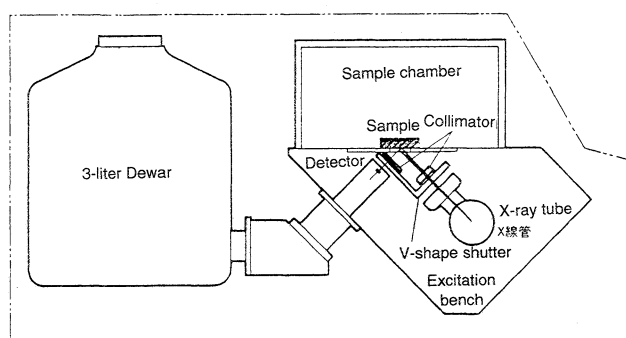


Fig.2 Cross-section of MESA-500 analyzer

3. Features of the MESA-500

The main development theme of the MESA-500 was to "develop a highly accurate element analyzer that can be used easily by anyone at any time." As a result the MESA-500 has the following features:

- ① All elements from Na to U can be quantitized by one-touch operation.
- ② Solids, liquids and powder samples can be measured in their original states without pre-processing.
- ③ Various protective mechanisms enable safe machine operation for the operator (automatic stop of X-ray generation, shutter interlocked with vacuum monitor, slow leak at vacuum cancel, etc.)
- ④ Degree of vacuum, X-ray tube voltage and current, etc. are automatically set to the optimum conditions according to sample.
- ⑤ Standard sample not required.
- ⑥ Liquid nitrogen is needed only at analysis.

Fig.3 shows the configuration of the MESA-500 system. **Table 1** shows the main specifications.

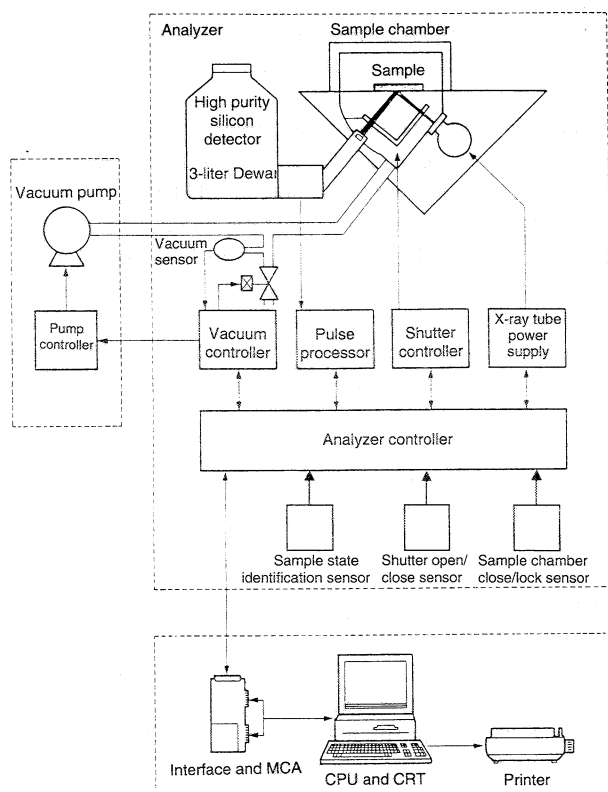


Fig.3 System configuration of MESA-500

Sample shape	Max. dia. 150 to 125 mm (varies according to sample thickness) Max. thickness 75mm
Sample chamber environment	Air, vacuum
Irradiation area	5mm dia.
X-ray tube target	Rh (Rhodium)
X-ray tube voltage	(1) 15kV (2) 50kV
X-ray tube current	1 to 500 μ A (15kV) 1 to 240 μ A (50kV)
Detector	High purity silicon detector XEROPHY
Dewar capacity	3 liters
Liquid nitrogen consumption	1 liter/day or less
Qualitative analysis	Automatic and manual
Quantitative analysis	(1) Fundamental parameter method (1) Standard-less (2) 1 point calibration (2) Calibration curve
Measurement condition settings	(1) Voltage: 15kV/50kV, automatic switching (manual possible) (2) Current: automatic adjustment (manual possible)
Program function	Automatic operation possible by memorization of operation procedure
Computer	IBM-PC/AT compatible 32-bit, 40 Mbyte hard disk, 3.5" floppy disk drive, OS: MS-DOS
Printer	Impact dot matrix, black ribbon
External output	RS-232C
Ambient temp.	10 to 35°C
Ambient humidity	20 to 80% (relative humidity)
Power supply	100, 120, 220, 240 V \pm 10%, 50/60Hz, 1kVA (Two grounded outlets are required as utilities.)
External dimensions (W x D x H)	Analyzer: 450 x 600 x 295mm Pump: 265 x 350 x 305mm
Weight	Analyzer: Approx. 55kg Pump: Approx. 13kg

Table 1 MESA-500 specifications

Below follows a detailed description of the element technology used for creating these features.

4. Ultra-Pure Silicon Detector

The MESA-500 uses an ultra-pure silicon detector. Up till now, a highly pure silicon single crystal doped with lithium for compensating for impurities was used in silicon semiconductor detectors. Recently, at HORIBA, we have succeeded in developing and commercializing¹⁾ the semiconductor detector XEROPHY that uses an ultra-pure silicon single crystal that does not require compensating. A feature of this detector is that it needs to be cooled by liquid nitrogen only during use and not during storage. It is one of the main reasons why energy dispersive X-ray detectors have come to be widely used in the field.

5. Automatic Qualitative Analysis

With conventional X-ray fluorescence analyzers, the elements in the sample were judged by verifying the peak position on the measurement spectrum with the fluorescent X-ray energy position for each element stored to analyzer memory in advance. However, diffraction peaks that occur in crystal samples, scattered peaks of characteristic X-rays in the X-ray tube target material, and fluorescent X-rays of other elements overlap with the peaks of the fluorescent X-rays of the object element, making it difficult to determine the element in a lot of cases. In such instances, the width of the peak and intensity ratio had to be taken into consideration in addition to the X-ray energy positions, and measurement results were highly reliant upon the analyst's knowledge of analyzers and samples.

As the MESA-500 allows anybody to simply carry out qualitative analysis, elements are automatically judged and displayed as follows:

- ① The degree of matching between the fluorescent X-ray energy positions and the peak positions on the measurement spectrum for all elements from Na to U is calculated as a value (M) from 0 to 100 and not simply by ON/OFF.
- ② M is calculated by taking into consideration the size of the measurement peak, difference between the measurement peak position and fluorescent X-ray energy position, and the weight due to the intensity ratio of fluorescent X-rays.
- ③ If M actually is greater than or equal to a, elements that can be judged are displayed as (exist), and elements that exist in slight amounts by $a > M \geq b$ are displayed as (?). Also, the values a and b are set empirically for each of the elements.

Automating this unique judgement operation has enabled anybody to carry out qualitative analysis with a fixed degree of accuracy.

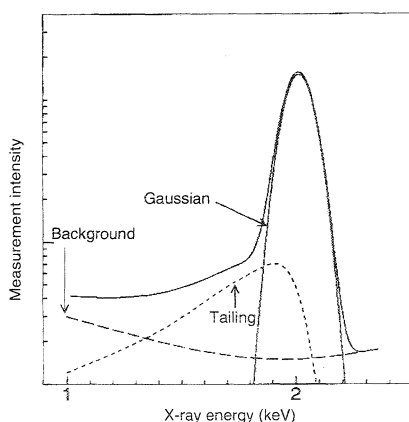


Fig. 4 Energy response function of a silicon detector

$$\begin{aligned} \text{Gaussian} &: \exp\{-(E-E_p)^2/(2\sigma^2)\} \\ \text{Background} &: a_0 + a_1 \cdot E + a_2 E^2 \\ \text{Tailing} &: \exp\{(E-E_p)/(B\sigma)\} [1 - \text{erf}\{(E-E_p)/(\sigma\sqrt{2}) + 1/(B\sqrt{2})\}] \end{aligned}$$

*2 Fluorescent X-rays of transition probability 1% or more

(K α_1 , K α_2 , K β_1 , K β_3 , K β_5 ,
K β_2 , L α_1 , L α_2 , L γ_1 , L β_2 ,
L β_6 , L β_{15} , L β_7 , L β_5 , L β_1 , L γ_1 ,
L γ_5 , L γ_8 , L β_3 , L β_4 , L γ_2 , L γ_3 ,
M α_1 , M α_2 , M ζ_1 , M ζ_2 , M β , M μ_4 -02,
M μ_3 -N1, M μ_3 -N4, M γ , M μ_3 -01, M μ_4 -02,
M μ_3 -04.5, M μ_2 -N4, M μ_1 -N2, M μ_1 -N3)

6. Spectrum Processing

Sometimes the energy resolution of energy dispersive X-ray fluorescence analyzers is not always sufficient for separating overlapping measurement peaks. In this case, spectrum processing for separating the overlaps and the background of fluorescent X-ray peaks becomes extremely important.

In order to separate and isolate only fluorescent X-rays and improve measurement accuracy, physical constants (peak position of fluorescent X-rays, emission probability of fluorescent X-rays, absorption edge, etc.), analyzer constants (energy resolution of detector, X-ray tube voltage, X-ray tube target material, etc.) and waveform information (background and peak functions) must be set before use.

6.1 Waveform information

As an energy response function of a silicon detector, the peak is approximated by Gaussian and tailing²⁾ formula, and background is approximated by a quadratic formula as shown in Fig.4. All peaks in the fluorescent X-rays listed in ASTM Data Series DS 46³⁾ having a transition probability of 1% or more*² are taken into consideration.

6.2 Spectrum processing procedure

Correction is carried out by subtraction or addition of the spectrum of the escape peak that is measured as X-rays of energy 1.74keV (fluorescent X-ray energy of silicon) lower than the energy of the X-rays incident to the detector. The overlap and background of fluorescent X-ray peaks are deconvoluted with respect to the spectrum that have undergone escape processing in order to extract the net intensity of fluorescent X-rays. Deconvolution is carried out in two stages as described below.

6.2.1 Calculation of initial values of deconvolution

First of all, the initial values of deconvolution are calculated. Waveforms having a fixed peak intensity ratio such as K α_1 , K α_2 and K β_1 for a single element are formed in advance. The measurement spectrum is combined with the waveforms of several elements and background, and the ratio of each element is calculated by the least-squares method so that the spectrum matches the waveform and background most, and this is taken as the initial value.

6.2.2 Deconvolution by negative restriction/non-linear least-squares fitting

Next, this initial value is used to deconvolute and isolate the peaks to the peaks required for quantitative analysis. In the measurement spectrum example (see Fig.5) for a sample containing Pt and Au, the peaks for PtL α_1 , L α_2 , L η , and AuL α_1 , L α_2 are isolated, and the fitting range is also narrowed. When calculating the initial value, the intensity ratio between peaks for a single element are fixed by the transition probability; however, these are made variable by negative restriction. The least-squares method is non-linear, and the solution is obtained by calculating the convergence of repeats by the Marquardt method⁴⁾. After each of the fluorescent X-ray intensity have been calculated, L α_1 and L α_2 are both taken as L α , and K α_1 and K α_2 are both taken as K α intensity for use in quantitative calculation.

7. Fundamental Parameter Method

Matrix compensation by the Fundamental Parameter Method (FPM) is a calculation for calculating the composition of the sample so that the measurement intensity measured by spectrum processing and the simulation intensity are matching. The simulation intensity is obtained by calculating the absorption effect by coexisting elements and the effect of secondary excitation from (i) analyzer constants such as the distance between the X-ray tube and sample, and the angle of the X-rays incident on the sample, (ii) physical constants such as the probability of emission of fluorescent X-rays, and (iii) the composition of the measurement sample.

This calculation is started assuming an initial value due to the fact that the composition of the sample to be finally calculated is required, and is a repeat calculation by which convergence is successively carried out. The physical constants required for calculation include primary X-rays⁵⁾⁶⁾, mass absorption coefficient⁷⁾, fluorescent X-ray energy³⁾, transition probability⁶⁾⁸⁾, fluorescent yield⁸⁾ and jump factor⁸⁾. The fundamental coefficient method⁸⁾ proposed in 1986 by N.Broll is used as the method for calculating convergence. Fig.6 shows the flow of calculation of FPM, and formula (1) shows the calculation formula.

$$C_i = R_i \times (1 + \alpha_{ij} \times C_j + \alpha_{ik} \times C_k + \dots) \quad (1)$$

$$R_i = \frac{P_i + \sum_j S_{ij}}{P_{i,i}}$$

$$\alpha_{ij} = \frac{qE_i C_i \int_{\lambda_{abs,i}}^{\lambda_0} \left\{ \frac{\mu_{i,\lambda} I_{\lambda}}{\mu_{s,\lambda} + A\mu_{s,\lambda}} \left(\frac{\mu_{j,\lambda} + A\mu_{j,\lambda}}{\mu_{i,\lambda} + A\mu_{i,\lambda}} - 1 \right) \right\} d\lambda}{P_i}$$

$$- \frac{S_{ij}/C_j}{P_i} \times \frac{qE_i C_i \int_{\lambda_{abs,i}}^{\lambda_0} \frac{\mu_{i,\lambda} I_{\lambda} d\lambda}{\mu_{i,\lambda} + A\mu_{i,\lambda}}}{P_i + \sum_j S_{ij}}$$

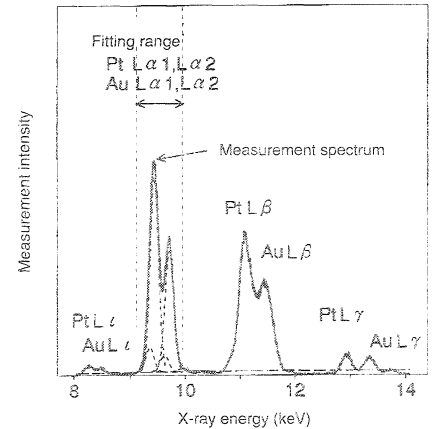


Fig. 5 Example of deconvolution by negative restriction/non linear least square fitting

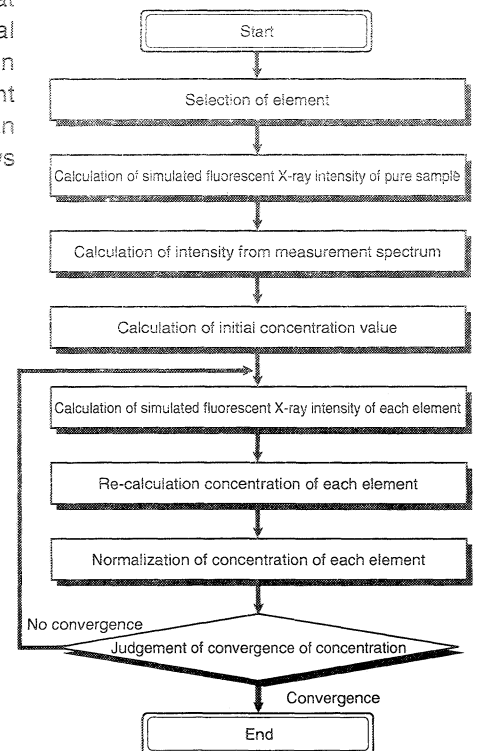


Fig. 6 Flow of calculation of FPM

$$P_i = q E_i C_i \int_{\lambda_{abs,i}}^{\lambda_0} \frac{\mu_{i,\lambda} I_\lambda d\lambda}{\mu_{s,\lambda} + A \mu_{s,\lambda i}}$$

$$S_{ij} = \frac{1}{2} q E_i C_i \int_{\lambda_{abs,j}}^{\lambda_0} E_j C_j \mu_{i,\lambda_j} L \frac{\mu_{i,\lambda} I_\lambda d\lambda}{\mu_{s,\lambda} + A \mu_{s,\lambda i}}$$

$$L = \frac{\ln \left(1 + \frac{\mu_{s,\lambda} / \sin \psi_1}{\mu_{s,\lambda j}} \right)}{\mu_{s,\lambda} / \sin \psi_1} + \frac{\ln \left(1 + \frac{\mu_{s,\lambda i} / \sin \psi_2}{\mu_{s,\lambda j}} \right)}{\mu_{s,\lambda i} / \sin \psi_2}$$

$$A = \frac{\sin \psi_1}{\sin \psi_2}$$

$$q = A \times \frac{d\Omega}{4\pi}$$

$$\mu_{s,\lambda} = \sum_i C_i \mu_{i,\lambda} \quad \mu_{s,\lambda i} = \sum_i C_i \mu_{i,\lambda i}$$

- R_i ... Intensity ratio of fluorescent X-ray λ_i of element i taking pure same as reference
- α_{ij} ... Coexistent element influence coefficient
- C_i ... Mass fraction of element i
- $P_{i,1}$... Intensity of fluorescent X-ray λ_i of element i in case of pure sample
- P_i ... Primary excitation fluorescent X-ray intensity of fluorescent X-ray λ_i of element i
- S_{ij} ... Secondary excitation fluorescent X-ray intensity of fluorescent X-ray λ_i by fluorescent X-ray λ_j of element j
- ψ_1, ψ_2 ... Primary X-ray angle of incidence, fluorescent X-ray detection angle
- E_i ... Excitation factor (value specific to each fluorescent X-ray λ_i)
- $\mu_{s,\lambda}$... Mass absorption coefficient of sample s on primary X-ray λ
- $\mu_{s,\lambda i}$... Mass absorption coefficient of sample s on fluorescent X-ray λ_i
- $\mu_{i,\lambda}$... Mass absorption coefficient of element i on primary X-ray λ
- I_λ ... Primary X-ray intensity
- λ_0 ... Highest energy of primary X-ray
- $\lambda_{abs,i}$... Absorption edge energy correspondent to fluorescent X-ray λ_i of element i

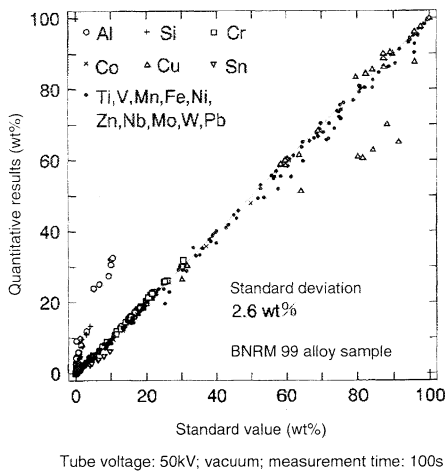


Fig.7 Standard-less quantity analysis of BNRM99 alloys: before correcting primary X-ray

8. Correction of Primary X-ray

The primary X-rays emitted from the X-ray tube consist of continuous X-rays and characteristic X-rays, and the excitation efficiency of each element varies greatly according to their energy distributions. For this reason, it is important that the primary X-ray used for calculating simulation and the X-ray generated at the actual analyzer match.

First of all, primary X-rays obtained by increasing the kind of the characteristic X-rays to those proposed by Pella et al⁵⁾. based on NBS Frame C⁶⁾ were used. **Fig.7** shows the results of standard-less quantitative analysis carried out without calibrating for sensitivity, etc. by FPM using the primary X-rays on the spectra of the BNRM99 alloy sample. Though this graph contains data for almost 900 points, the error is conspicuous for Al, Cu and Sn. In particular, the error of Cu alloy, in which a relatively lot of elements with distant atomic numbers such as Al and Sn, is large.

A probable cause of this in addition to primary X-ray is the error in analyzer constants and physical constants. However, an attempt was made as to whether or not all these can be corrected by correcting only primary X-ray. Namely, the primary X-rays were corrected so that the simulation intensity of fluorescent X-rays matches the actual measurement intensity.

Fig.8 shows the results of standard-less quantitative analysis using corrected primary X-rays. The error of Al, Cu and Sn has been reduced, the standard deviation is now 0.39wt%, and quantitative accuracy has improved considerably.

9. Multiple Condition FPM

In order to further improve accuracy, the MESA-500 has been designed so that a single sample is measured while varying the voltage of the X-ray tube to obtain more accurate quantitative results from multiple data sets. As the detection sensitivity of elements differs greatly with atomic number and excitation X-ray energy, this method is a clever method of avoiding measurement where either of the two types of elements is insufficient at only one tube voltage in samples where light elements coexist with heavy elements.

For example, in the case of a sample where a light element such as Al coexists with an element having a relatively large atomic number such as Cu, if the tube voltage is lowered in order to increase the accuracy of Al, the accuracy of Cu will be reduced; alternately, if the tube voltage is raised in order to increase the accuracy of Cu, the accuracy of Al will be reduced. For this reason, in FPM quantitative calculations where the results of quantitative measurement of all elements are used as the information, inevitably this caused a drop in overall accuracy.

For this reason, we developed multiple condition FPM (see **Fig.9**) for calculating the mutual interference of coexisting elements from measurement data caused by multiple tube voltages, and have improved quantitative accuracy.⁹⁾

Fig.9 below shows by calculations and data how quantitative accuracy is improved by this method.

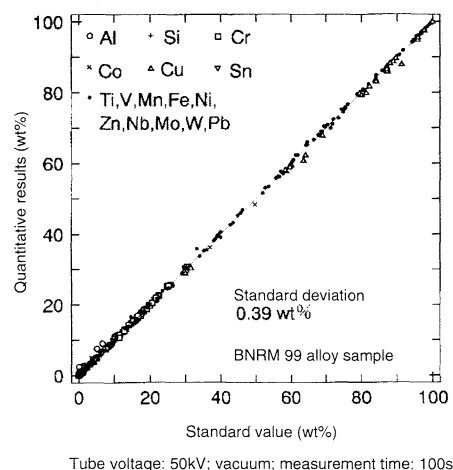


Fig.8 Standard-less quantity analysis of BNRM99 alloys: after correcting primary X-ray

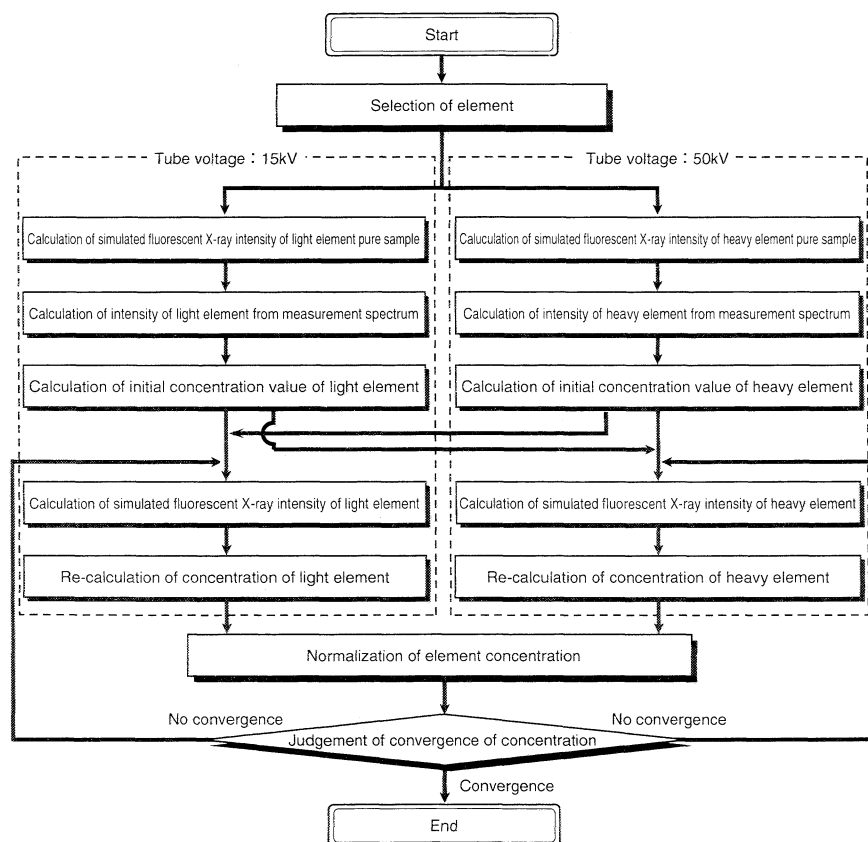


Fig.9 Flow of calculation of FPM by automatic switching of tube voltage

9.1 Relationship between tube voltage and minimum detection limit

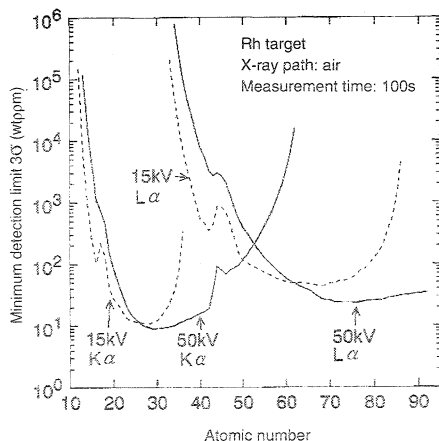
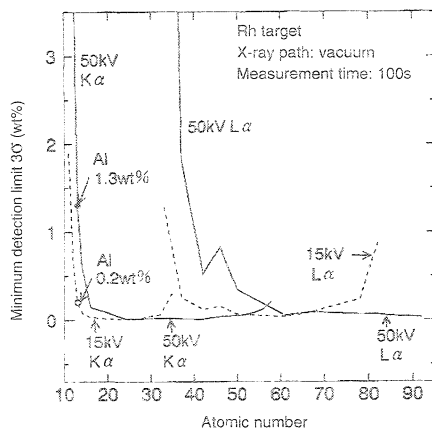


Fig.10 Minimum detection limit of water-soluble sample (calculated value)

15/50kV: adjusted to same DT% by tube current



Calculation when each fluorescent X-ray does not overlap other fluorescent X-rays and diffraction peaks, etc.

Fig.11 Minimum detection limit of alloy sample (calculated value)

15/50kV: adjusted to same DT% by tube current

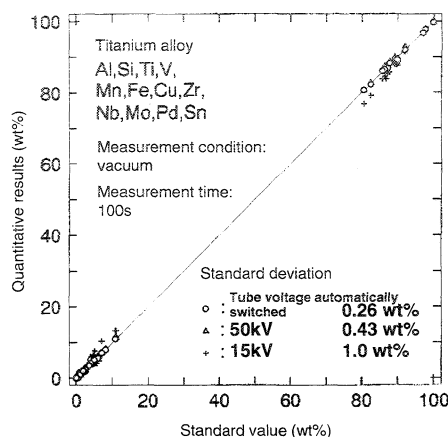


Fig.12 Standard-less determination of MBH Analytical Ltd., titanium alloys (101P): after correcting primary X-ray

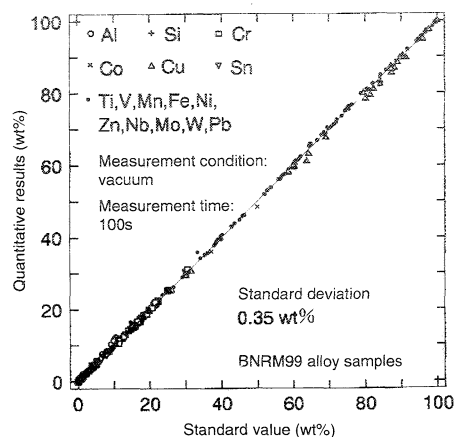


Fig.13 Standard-less determination of BNRM99 alloys: automatically switched X-ray tube

Fig.10 shows the calculated values for the minimum detection limit when a water-soluble sample is measured using tube voltages of 15kV and 50kV. The tube current is adjusted so that the appropriate counting rate can be achieved at each of the tube voltages, and the tube current for tube voltage 15kV is about 20 times that of the tube current for tube voltage 50kV. When measuring elements of atomic number up to 20, tube voltage 15kV exhibits a minimum detection limit one digit better than that of tube voltage 50kV; alternately, with elements of atomic number 30 or greater, tube voltage 50kV exhibits a minimum detection limit one to two digits better than that of tube voltage 15kV.

Fig.11 shows the calculated values for the minimum detection limit when a Cu alloy sample is measured. Likewise, the tube current is adjusted so that the appropriate counting rate can be achieved at each of the tube voltages, and the tube current for tube voltage 15kV is about 10 times that of the tube current for tube voltage 50kV. For Al, when the tube voltage is 50kV, the minimum detection limit is 1.3wt%, and the minimum detection limit is 0.2wt% when the tube voltage is 15kV, which indicates a difference of about six times.

9.2 Tube voltage and standard-less quantitative accuracy

Fig.12 shows the results of measuring 14 titanium alloy samples from MBH Analytical Ltd. by standard-less measurement. As both Al and Sn coexist at relatively high concentrations, this sample demonstrates well the effect of multiple FPM. The samples were measured in three ways (tube voltage 15kV, 50kV, automatically switched) for 100 seconds each. Note, however, that when the tube voltage is automatically switched, multiple condition FPM of 50-second measurement at 15 kV after 50-second measurement at 50kV was carried out.

The standard deviation is 1.0wt% at a tube voltage of 15kV, 0.43wt% at 50kV, and 0.26wt% during automatic switching of the tube voltage, which indicates improved quantitative accuracy.

Fig.13 shows the results of standard-less quantitative analysis of BNRM99 alloys with automatic switching of the tube voltage. Even though few of the samples contained light element Al, the standard deviation was 0.35wt%, which indicates improved accuracy.

10. Conclusion

This paper has described in detail the content of quantitative calculations carried out at the MESA-500, and has demonstrated that multiple condition FPM improves quantitative accuracy. This is not an issue of only calculation, but a problem that has emerged for the first time with technological advances made in hardware such as the stability of tube voltage, accuracy of the ratio of the tube currents that vary by up to 500 times according to the sample and tube voltage, and accuracy of deadtime correction in pulse processing. Though the measurement accuracy of fluorescent X-rays is influenced by many parameters including the concentration of coexisting elements, all parameters can be calculated and processed by increasing the memory and increasing processing speed of the personal computer, and operation has been made simpler, and precision has been improved. The technology applied in hardware such as excitation source, optical system, and detector has advanced steadily. Accompanying higher grade calculation processing, we believe that X-ray fluorescence analyzers that are easy-to-use, compact, and highly accurate will be all the more familiar to us in the future.

Reference

- 1) Shigetoshi Arai, "The XEROPHY: A High-Purity Si X-ray Detector" Readout-HORIBA Technical Reports-, No.2, p.49-56 (1991).
- 2) M. Krumrey, E. Tegeler and G. Ulm "Complete characterization of a Si(Li) detector in the photon energy range 0.9-5keV" Rev. Sci. Instrum. 60(7), July p.2287 (1989).
- 3) G.G. Johnson, Jr., and E.W. White "X-RAY EMISSION WAVELENGTHS AND KEV TABLES FOR NONDIFFRACTIVE ANALYSIS" ASTM Data Series DS 46 (1970)
- 4) Takashi Awaya, "Data analysis: Analog and Digital" Gakkai Shuppan Center (1985) p.130-135.
- 5) P.A. Pella, Liangyuan Feng and J.A. Small "An Analytical Algorithm for Calculation of Spectral Distributions of X-Ray Tubes for Quantitative X-Ray Fluorescence Analysis" X-RAY SPECTROMETRY, VOL. 14, NO.3, p.125 (1985).
- 6) R.L. Myklebust, C.E. Fiori and K.F.J. Heinrich "Frame C: A Compact Procedure for Quantitative Energy-Dispersive Electron Probe X-ray Analysis" National Bureau of Standards Technical Note 1106, 111 pages (Sept. 1979).
- 7) Tran Phuc Thinh, Jean Leroux "New Basic Empirical Expression for Computing Tables of X-Ray Mass Attenuation Coefficients" X-RAY SPECTROMETRY, VOL.8, NO.2, p.85 (1979).
- 8) N. Broll "Quantitative X-Ray Fluorescence Analysis. Theory and Practice of the Fundamental Coefficient Method" X-RAY SPECTROMETRY, VOL.15, p.271-285 (1986).
- 9) A. Kira, Y. Okada, M. Pohl, "A New Development in Energy Dispersive X-ray Fluorescence" PITTCON '93 (USA).