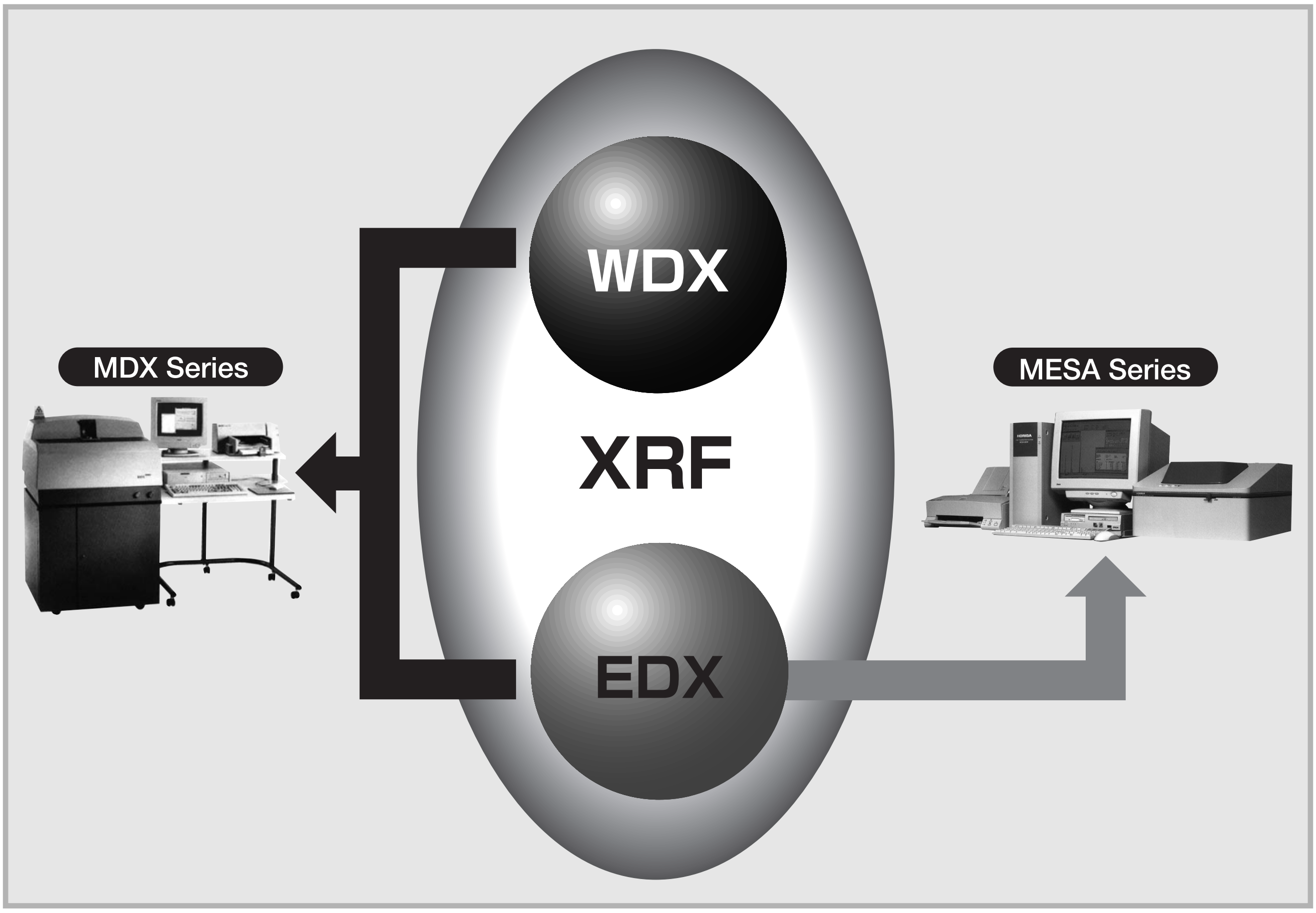
FEATURE ARTICLE

Versatile Multi-Element Analysis Using X-ray Fluorescence The MESA-500 Series and The MDX-1000 Series

Akimichi KIRA, Neal ROBSON*

*Oxford Instruments plc.



Abstract

Recent years have witnessed rapidly growing needs for the precise elemental analysis of steel, ceramics, organisms, foods, and other materials in various fields, and considerable attention has been focused on X-ray fluorescence element analyzers. As the market for these analyzers expands, demand is also growing for new features that allow easy access by any user in addition to the excellent features of X-ray fluorescence spectroscopy, which enable non-destructive analysis with minimal or no sample preparation. Horiba, Ltd. has released the MESA-500 series of element analyzer products, focusing on the ultimate target of usability based on EDX. Oxford Instruments plc has put on the market the MDX-1000 series of element analyzers, which pack the features of both EDX and WDX in a compact instrument . This article provides an introduction to the features and applications for each of these product series.

1 Introduction

XRFS (X-ray fluorescence spectroscopy) refers to analytical methods characterized by simple or no sample preparation and the non-destructive, high-speed qualitative and quantitative analysis of many kinds of elements in a wide range of concentrations.

XRF systems are grouped into two major types: wavelength-dispersive X-ray fluorescence (WDX) and energy-dispersive X-ray fluorescence (EDX). In WDX, X-rays are irradiated toward a given sample in a vacuum or helium-filled atmosphere. The generated characteristic X-rays are separated into each components by the monochrometor, and elements in the sample are detected by a proportional counter or NaI scintillator. Analysis must be done for each individual element. With EDX, on the other hand, generated characteristic X-rays can be guided directly to a semiconductor X-ray detector where the energy levels are separated, so many elements can be analyzed simultaneously.

Highly sensitive WDX analyzers, which also require handling expertise, are used mainly for high-precision element analysis. Compact, easy-to-handle EDX analyzers, on the other hand, are used mainly as versatile multi-element analyzers.

Horiba has put on the market various EDX-type X-ray fluorescence element analyzers under the "MESA Series" name, and has established a wide customer base in many fields. Oxford Instruments has released to the market multi-dispersive X-ray fluorescence element analyzer products (MDX Series) which features both WDX and EDX packed incorporated into one instrument. These two companies are planning to expand the range of new applications for their X-ray fluorescence element analyzers. Table 1 shows the features of EDX, WDX, and MDX.

Principle	EDX	WDX	MDX
Elements	Na-U	Be-U	C-U
Measurement mode	Simultaneous	Sequential(Scanning type) or Simultaneous(Fixed type)	Simultaneous(Fixed type)
Analysis area	ϕ 1-10mm	ϕ 10-35mm	ϕ 20mm
Detection limit *1			
heavy matrix *1-1	100-1000 ppm	5-50 ppm	10-100 ppm
intermediate matrix *1-2	10-100 ppm	1-10 ppm	2-20 ppm
light matrix *1-3	1-20 ppm	0.2-2 ppm	0.5-5 ppm
Utility			
Cooling water	unnecessary	required	unnecessary
Liquid nitrogen	unnecessary or required	unnecessary	unnecessary
PR gas	unnecessary	required	required

*1 Detection limit in measering of Ti~Cu (depend on each instrument)
*1-1 Typical heavy matrix material : Steel
*1-2 Typical intermediate matrix material : Cement
*1-3 Typical light matrix material : Plastics

Table1 The features of EDX, WDX, and MDX

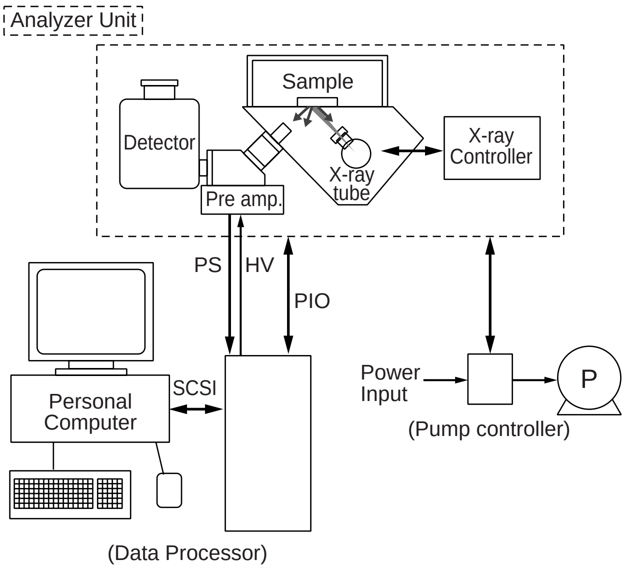
2 The MESA-500 Series

2.1 Instrument Configuration

MESA-500W is an energy-dispersive X-ray fluorescence element analyzer with the capability of analyzing element type and components in solid, powder, liquid, or any other sample form, at high speed and precision and without damaging the sample. The MESA-500W also requires no standard samples.

The MESA-500W analyzer consists of an analyzer unit, a data processing unit, a vacuum pump, and a computer. Air-cooled X-ray tube suited for EDX spectroscopy, a high-purity silicon X-ray detector that requires no supply of liquid nitrogen during storage, a power supply for the X-ray tube, and a high-precision current and voltage control circuit for the power supply are compactly arranged in the analyzer unit. The data-processing unit is composed of a high-rate pulse-processing circuit that measures detector signals, and a user interface. The computer is pre-installed with a Windows® operating system and dedicated MESA-500W software, which provides easy access to spectrum analysis, automatic qualitative analysis, and quantitative analysis using fundamental parameters and calibration methods. Fig.1 shows the the MESA-500W and its system configuration.

a) MESA-500W



b) System configuration of the MESA-500W

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

2.2 Features and Functions

The MESA-500W analyzer incorporates various features that enable the user to perform high-precision, high-efficiency analytical work with simple operations, in addition to the fundamental features of EDX spectroscopy that are used to analyze solid, liquid, or powder samples. As a result, any operator can perform qualitative and quantitative analyses of a wide range of elements without any special preparation of unknown samples.

(1) Quantitative analysis without standard samples

The MESA-500W analyzer can perform precise quantitative analysis with no preparatory work such as calibration using standard samples and the pre-registration of a standard spectrum. It can separate overlapping peaks and the backgrounds of the X-ray spectrum and calculate the precise intensity of the fluorescent X-rays using the non-negative-constraint and non-linear least square method, which utilizes the energy response functions of the detector. The MSEA-500W also has the capability to conduct the quantitative analysis of a wide range of elements.

(2) Automatic qualitative analysis

Press the automatic qualitative analysis button, and the MESA-500W analyzer will display the element symbols of elements likely to be contained in a given sample, with the symbols shown at their corresponding positions in the fluorescent X-ray spectrum. The contained elements will also be indicated in a periodic table. This feature helps operators with no special knowledge of the X-ray spectrum to quickly identify elements in the sample.

(3) Automatic switching of X-ray tube anode voltage

Spectral data measured at the high and low anode voltages of the X-ray tube is used in the calculations in the fundamental parameter method, thus enabling the precise quantitative analysis of samples which contain both low and high atmic number elements.

(4) Automatic adjustment of X-ray tube anode current

This feature automatically adjusts the anode current of the X-ray tube to the best value for a given sample. As generation efficiency of fluorescent X-rays differs greatly between metal and organic film sample (the best currents can vary by a factor of more than 100 between the two), the anode current must be set to the best value for the composition of each sample. This feature controls the anode current to set the dead time of the pulse circuit to the best value, and adjusts the intensity of the X-rays that are incident upon the detector.

(5) Automatic calibration

The MESA-500W analyzer also features automatic calibration using the maintenance sample included with the analyzer. This feature will calibrate the horizontal axis (energy) and the vertical axis (X-ray intensity) of the X-ray spectrum and will at the same time calculate the energy resolution of the detector used for spectrum analysis. It is recommended that the analyzer be calibrated once every two months.

2.3 Application

The MESA-500W analyzer has been used in various fields and applications, such as customhouse inspection and quality management at semiconductor plants. Fig.2 shows various applications of the MESA series.

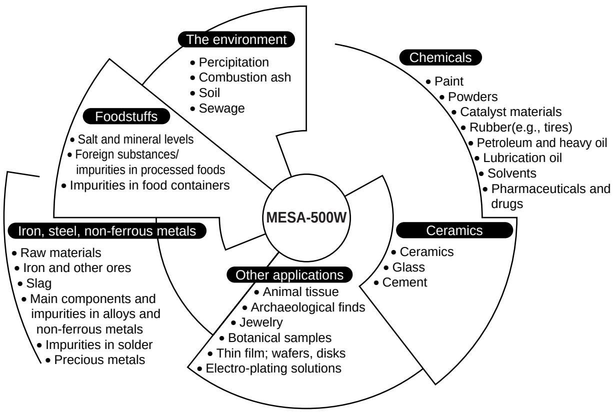
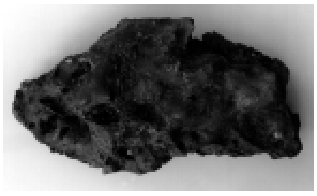


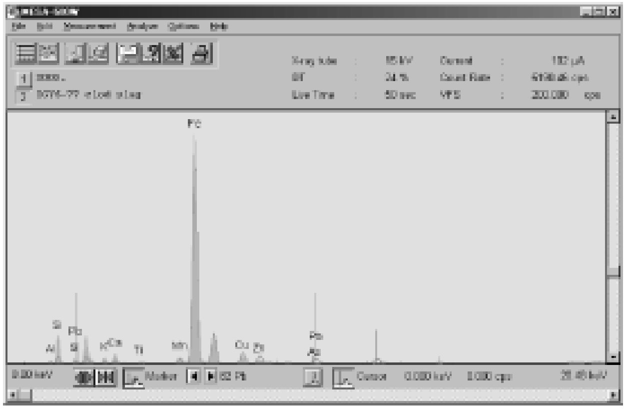
Fig.2 Various applications of the MESA series

The following is a description of how the MESA-500W was used to survey the remains of a copper smelting facility. In the remains of the copper mines in Taka County of Hyogo Prefecture, the MESA-500 was used to analyze the elements in more than 150 samples, including kiln pieces found in the upper earth layer (dating to the middle of the 19th century) and furnace pieces found in the lower earth layer (dating from the end of the 16th century to the first half of the 17th century). The instrument was used to analyze the composition of 5 primary elements, iron (Fe), silicon (Si), aluminum (Al), manganese (Mn) and potassium (K), as well as the secondary elements sulfur (S), arsenic (As), tin (Sn), copper (Cu) and lead (Pb), in the soil, slag, road stones, and vein stones left in the furnaces and tuyeres. It was also used to classify the smelting and to analyze the refining processes. The following findings were reported. Fig.3 shows the measured result of a clod slag using MESA-500W.[1)]

* Flat or clod slags, mineral powder or sauce, and clay obtained from the outer and inner walls of kilns and furnaces, can be grouped by the composition ratios of Fe, Al, and Si.
* A high level of arsenic (As) is contained in samples obtained from the kilns. (This indicates that As was oxidized and removed in the kilns.)
* Levels of Ca differ greatly by groups, indicating that Ca was used selectively as a slag forming reagent.
* Different compositions of furnace-wall clay suggest that smelting processes ranging from calcination to crude copper production were used in the time period corresponding to the lower-layer, and processes ranging from calcination to the smelting of silver and copper were used in the time period corresponding to the upper-layer.



a) Clad slag



b) A screen of the measurements

Fig.3 Measured result of a clod slag using MESA-500W[1)]

3 The MDX-1000 Series

The compact, fully integrated MDX (Multi-Dispersive X-ray fluorescence) series of spectrometers provides the capacities for both EDXRF and WDXRF analysis in a single instrument. (Fig.4) This combines the flexibility and range of EDXRF with the higher resolution (for lower atomic number elements) and speed of WDXRF. Modular construction enables a choice of configurations to meet different needs.

Fig.4 Multi-Dispersive X-ray fluorescence element analyzer MDX-1000

3.1 Instrument Composition

The core of an MDX Spectrometer is the X-ray tube, multiple detection channels, and digital pulse processor (Fig.5).

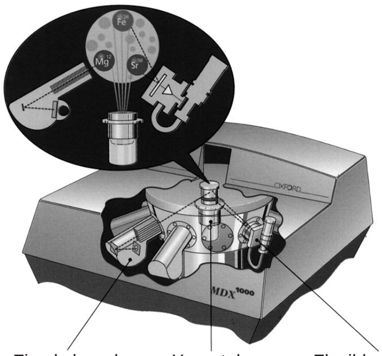


Fig.5 System configuration of the MDX-1000

Simultaneous WDXRF provides the fastest possible analysis for routine analysis of known elements, with low detection limits. The MDX-1060 can be fitted with multiple monochromators for simultaneous WDX analysis of up to 12 elements. Each detection channel, or monochromator, consists of a collimator, crystal and proportional detector selected and set for the characteristic X-rays of a particular element. For example, the monochromator for sulfur analysis consists of a collimator, germanium crystal and argon methane detector which together are set to a "Bragg angle" of 110.7 degrees (2 theta) corresponding to a (sulfur) wavelength of 0.5373 nm.

For flexibility, or analysis of unknown elements (e.g. contaminants), the MDX-1080 can be configured with a solid state Energy Dispersive channel alongside the fixed channels, which uses EDXRF analysis to collect the spectrum of up to 50 elements, allowing rapid qualitative and quantitative analysis. For example, a semi-quantitative analysis of unknowns can be made automatically from the data library of element reference values. The combined technique allows each system to operate in its optimum range, i.e. wavelength dispersive for the measurement of low atomic number elements (Mg, Al, Si, S etc), where resolution is paramount, and energy dispersive for medium/high atomic numbers, where low backgrounds are particularly important.

3.2 Features and Functions

The use of a digital pulse processor with the energy dispersive channel allows high count-rates (up to 100,000 cps), reducing analysis time and increasing sample throughput.

The compact medium-power X-ray tube, which uses a rhodium target, underpins the performance of the whole system, operating continuously at 200 watts. It is positioned below the sample to allow the analysis of liquids. (A secondary safety window can be fitted to avoid any sample leakage entering the spectrometer.) An automatic, integral temperature control maintains the spectrometer at 37°C, without the need for an external cooling system, or its associated plumbing.

Sample preparation is minimal. Liquids are poured into a sample cell, powders are pressed into pellets, and metals only require grinding or turning to a flat surface.

The flexibility of the MDX spectrometers is made extremely accessible to a wide range of users through the *XpertEase* Windows®-based user interface. All functions, including selection for single or multiple samples, analysis of unknowns, and method set-up, are requested using easily identified click-on buttons. Fig.6 shows a screen for setting up semi-quantitative analysis of unknowns.

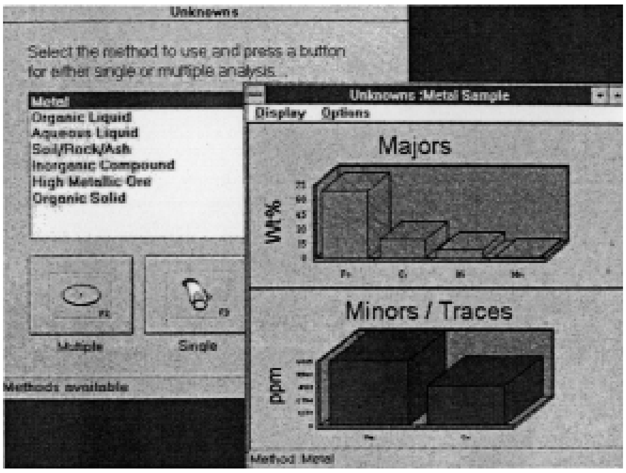


Fig.6 A screen for setting up semi-quantitative analysis of unknowns

Some of the features available include:

* Sample spinner for inhomogeneous sample analysis.
* Unattended operation - using the autosampler, up to 72 preloaded samples may be analysed without operator intervention.
* Multitasking - new data may be entered during automatic sample analysis.
* Priority interrupt - high priority samples may be inserted for individual analysis during automatic runs.
* Password control - different users may be given different levels of access.

3.3 Application

A typical application of an MDX-1000 spectrometer is the determination of levels of sulfur (S), nickel (Ni), and vanadium (V) in fuel oil, the thick residual material resulting from the refinery distillation of crude oil. Fuel oil is the primary component for all grades of petrol (gasoline), diesel fuels for both motor vehicles and railway locomotives, aviation fuels, and finally heavy residual oils for marine diesel engines and power stations. During combustion, nickel and vanadium can form compounds that are corrosive to metal. At trace levels in petroleum they can deactivate catalysts during processing. Levels of sulphur are regulated because of its environmental impact. Using the Oxford Instruments' MDX-1060 wavelength dispersive X-ray fluorescence spectrometer, fitted with four monochromators one used for the automatic subtraction of background signsls, the rapid, simultaneous analysis of these three elements gives excellent results (Table 2).

Analyte	Conc. range	Calibration standard error	Limit of detection (3sigma)	Mid-range precigion (95%confidence)
S	0.1-1.0%	0.002%	0.002%	0.007%
Ni	0-50mg/kg	0.4mg/kg	1mg/kg	<1mg/kg
V	0-50mg/kg	0.5mg/kg	1mg/kg	<1mg/kg

Table 2 Specifications of the MDX-1060

4 Conclusion

This paper covers the specifications and some applications of the MESA-500 series analyzers. The ultimate goal in the design of these analyzers is to achieve simplicity, usability, and a compact instrument body for EDX spectroscopy. We have also looked at the MDX-1000 series spectrometers, which incorporate features of both EDX and WDX spectroscopy. These two series can perform non-destructive element analysis, a feature of X-ray fluorescence element analyzers, and they each have their own specialized functions and software features as well. By entering into a business alliance, Horiba and Oxford Instruments now have even greater capacity for providing products optimized to their customers' needs. We shall continue efforts to promote communications with our customers so as to be able to meet their on-going and changing needs.

Reference

1) Research of the history of copper produced in Harima area, Investigation Committee of the ruins around Mount Myoken (July 4, 1999)

Akimichi KIRA

Scientific Instruments R&D Dept.
Horiba, Ltd.

Neal ROBSON

Marketing Manager-XRF
Oxford Instruments plc.