A SI/LI BASED HIGH RESOLUTION PORTABLE X-RAY ANALYZER FOR FIELD SCREENING OF HAZARDOUS WASTE

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INTRODUCTION

Only four years have passed since the first publication describing the application of a portable x-ray analyzer, (XRF), for on-site chemical characterization of contaminated soil [1].

During that period, field portable x-ray fluorescence (FPXRF) has established itself as the most useful technique for a broad range of environmental applications. Its well known attributes such as ruggedness, nondestructiveness, minimal sample preparation and speed of analysis are indisputably the factors contributing to its growing success. However, it was technological advances in the proportional detector (high resolution) and in microprocessor technology (computing power and portable architecture) which really made feasible a small, truly portable, battery operated device with analytical capabilities similar to the laboratory XRF systems.

FPXRF ANALYZER CONCEPT

The most successful implementation of the FPXRF for the on-site screening and analysis of inorganics in hazardous waste is based on the aforementioned microprocessor controlled analyzer connected to a hand-held probe.
The probe contains an x-ray source(s), a detector and a means of reproducible presentation of the sample for measurement. The electronic unit accepts the signal from the probe, processes it and displays the result. It also contains power supplies and interfaces for communicatiion with the operator and peripheral devices.

A sealed radioisotope capsule emitting x-ray or low energy gamma rays is a preferred source of primary radiation for portable instruments. Such sources are rugged, compact, light weight and drift free.

A high resolution, gas filled proportional detector has been for years an integral part of the most successful FPXRF analyzer available, the X-MET 880. Its much improved energy resolution of 10 to 12% as compared with conventional proportional counters (20%), made possible abandonment of mechanical means of element separation (so called nondispersive XRF, using a pair of balanced filter for each measured element) in favor of energy dispersive XRF, based on electronic separation of elements according to their characteristic x-ray energies. More recently, the probe of the analyzer has been modified to accept two excitation sources and thus has extended the range of elemental analysis of the probe.

Fig. 1. **FPXRF Analyzer X-MET 880 with a gas filled detector probe.**

QUANTITATIVE ANALYSIS

Quantitative analysis is accomplished by employing empirical calibration methods. Usually a set of 15 to 20 samples is required to develop calibration curves for up to six analytes per calibration program (model). The instrument can quantify six elements in each of its 32 calibrationh models. Availability of calibration samples may pose a problem especially in situations where not much is known about the site to be analyzed. Since XRF technique, it is important that the calibration samples match in matrix composition the unknown samples to be analyzed. This condition can rarely be met, although the most accurate results have always been obtained when the analyzer was calibrated with CLP analyzed samples collected on the site to be investigated (so called site specific calibration samples). An alternative solution is calibration of the analyzer with a set of spiked soil samples, so called site typical samples [2]. This approach results usually in a systematic error (bias) in the XRF measurements. However, it can be easily corrected as it is a common practice to submit 10 to 20% of all samples measured on the site with the FPXRF for verification by contract laboratory program (CLP) analysis. By correlating the XRF with the CLP results one is able to correct for the bias in the remainder of the XRF results.
This approach has been successfully used for screening and preliminary evaluation of levels of contaminats on a number of sites where FPXRF could be accepted as a Level I analytical method (that is inaccuracy up to +/- 50% relative and precision up to +/- 10% relative) [3].

HIGH RESOLUTION SI/LI PROBE

While the FPXRF analyzer configuration, described above enables one to reach detection limits down to 100 to 200 mg/kg for elements such as Cu, Zn, Pb, As, etc. [2], it has demanding calibration requirements when handling the diverse sample matrices common in analysis of hazardous waste. To address this problem a new, Si/Li based, hand-held probe was designed. The probe combines unsurpassed energy resolution with portability and ease of operation.

The heart of the probe is a Si/Li detector featuring 30 mm^2 active area and an energy resolution better than 170 eV for the K-alpha line of manganese at 1000 cps.
The detector is cooled by a small

LN_2 capacity with a holding time of 8 hours. Dewar construction enables operation of the probe in <u>any</u> position making it truly portable. There were no adverse effects observed due to thermal cycling of the probe. The probe can accommodate two radioisotope sources to cover the elemental range from K to U.

Fig. 2. A prototype Si/Li probe.

The probe is equipped with interlock mechanisms which prevent source exposure and high voltage supply to the detector, whenever the amount of LN_2 in a dewar is not sufficient. The probe can be easily set-up directly on the soil surface for true in-situ measurements, or it can be, after turning it over, used as a sample probe to measure samples presented in cups.

Perhaps the most important feature of the probe is that it can be used directly with the existing population of X-MET 880's. The Si/Li probe is therefore a useful addition to the many types that already are used with this analyzer.

Fig. 2 shows a photograph of the prototype Si/Li probe.

PROBE PERFORMANCE

The advantage of the state-of-the-art energy resolution of the probe can be seen in Fig. 3. The figure shows two simulated spectra as would be generated in a sample with Cr to Fe concentration ratio of 1 to 20.

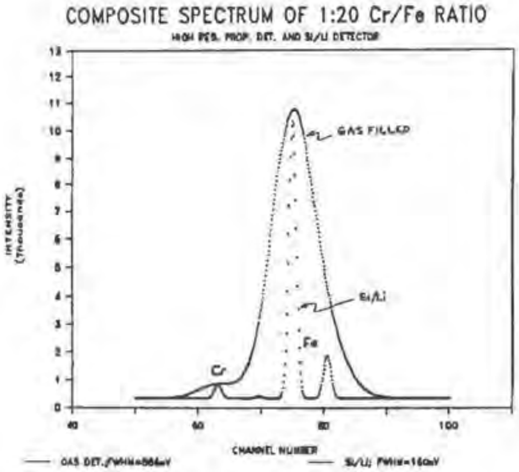

Fig. 3. Comparison of detector resolution.

It is clear that with a Si/Li detector it is possible to distinguish a minor Cr peak from a massive Fe peak, whereas even with a high resolution proportional detector such a faint Cr peak can hardly be seen.

Fig. 4 illustrates a typical soil spectrum excited with a Cd-109 source and collected with the Si/Li probe connected to the X-MET 880 FPXRF analyzer.

As expected, all peaks are clearly resolved except for the notorious pair of As K-alpha and Pb L-alpha. However, it is important to note that the resolution of the detector is not the only parameter determining its overall performance. For example, a gas proportional detector has much higher detection efficiency than a small Si/Li diode. This is due to the fact that a typical proportional counter collects radiation from a much larger solid angle than a typical Si/Li detector. However, a

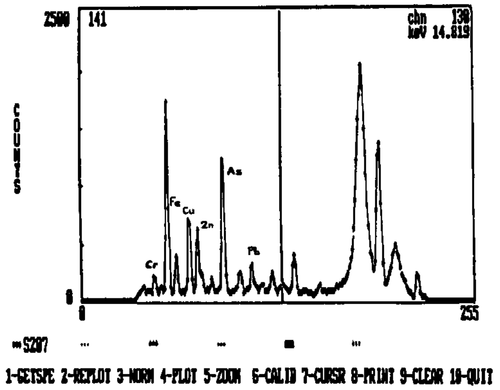

Fig. 4. Spectrum of soil sample.

proportional counter will usually exhibit also a higher background which somewhat offsets its efficiency advantage. The improvement in sensitivity and detection limits achievable with a Si/Li detector comes mainly from the low background of this detector.

Although the proportional detector exhibits excellent performance with conditions of optimal separation of more than Z+2 atomic number spread, when adjacent elements (or overlapping spectral lines) are present, enhanced resolution is of importance. In such cases of severe spectral overlap and unfavorable ratio of analyte concentration to interfering matrix element the resolution factor plays a critical role.

Another important implication of superb energy resolution is the ability to separate coherent and incoherent backscatter peaks of primary radiation. This enables one to implement a more sophisticated data treatment, such as those based on a fundamental parameters approach, which can better handle a diversity of sample matrices.

At present, the Si/Li probe can be used directly with the X-MET 880 in an empirical calibration mode. An extensive development program is being completed to implement a fundamental parameters based mode, initially in a PC connected to the FPXRF analyzer via its serial port.

Typical detection limits obtained with a Si/Li probe for a multielement matrix such as Cu, Zn, As, Pb are on the order of 30 to 80 mg/kg as opposed to a 100 to 200 mg/kg with a gas filled proportional detector.
Further work is in progress to further refine the final probe design and mathematical algorithms for data treatment. These results will be reported in the near future.

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[2] Piorek S. and Rhodes J.R. - "A New Calibration Technique for X-Ray Analyzers Used in Hazardous Waste Screening", Proc. 5th Natl. Conf. on Hazardous Wastes and Hazardous Materials, pp. 428-433, HMRCI, Silver Spring, MD, 1988.

[3] "U.S. EPA Data Quality Objectives for Remedial Response Activities Development Process", EPA/540/G-7/003, US EPA Washington, D.C., 1987.

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