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WATER QUALITY MONITOR
(EMPAX INSTRUMENT)

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ABSTRACT

The impetus of the Viking Mission to Mars led to the first miniaturization of a X-ray Fluorescence Spectrometer (XRFS). Two units were flown on the Viking Mission and successfully operated for two years analyzing the elemental composition of the Martian soil. Under a Bureau of Mines/NASA Technology Utilization project, this XRFS design was utilized to produce a battery powered, portable unit for elemental analysis of geological samples. This paper will detail design improvements and additional sampling capabilities that have been incorporated into a second generation portable XRFS that was funded by EPA/NASA Technology Utilization project. The unit, known as EMPAX (Environment Monitoring with Portable Analysis by X-ray) was developed specifically for quantitative determination of the need of EPA and any industry affected by environmental concerns, the EMPAX fulfills a critical need to provide on-site, real-time analysis of toxic metal contamination. A patent has been issued on EMPAX, but a commercial manufacturer is still being sought.

INTRODUCTION AND BACKGROUND

In 1976, two miniaturized X-Ray Fluorescence Spectrometers (XRFS) were landed on Mars and successfully operated for over two years performing elemental analysis of Martian soil samples. These spectrometers were built for NASA by Martin Marietta and were part of the instrumented landers of the Viking Mission to Mars Project. These spectrometers used proportional counters for X-ray detectors, radioactive isotope sources as the X-ray generators and standard pulse height analysis for the electronics. This combination has served as the basis of all national and international space missions flown to date.

In 1979, NASA and Martin Marietta built a portable battery operated version of this instrument and delivered this prototype instrument to the Bureau of Mines for evaluation. Since then, several bench and portable versions are commercially available with the proportional counters/isotope source combination.

In 1979, at the request of EPA, NASA and Martin Marietta embarked on a feasibility study to determine if the portable X-Ray Spectrometer concept could be advanced to the point where sensitivities to a series of toxic metals in the range of parts per million (ppm) to parts per billion (ppb) in water samples could be achieved. Through the use of precipitating agents and collection of the precipitate on filtration membranes, sufficient preconcentration was obtained to achieve the majority of the elemental sensitivities desired using an X-Ray tube as the X-ray generator and a solid state, liquid nitrogen cooled Si(Li) detector as the X-ray sensor. Based on this information, funding was obtained to develop and deliver two prototype instruments for evaluation by NASA and EPA.

INSTRUMENT DEVELOPMENT AND DESIGN

In the development of a portable XRFS for the EPA, two decisions were made early in the program that directly affected the final instrument design. One was to have separate modules for the basic components rather than have them all incorporated into one combined instrument package and two was to use commercially available components wherever possible. Since the instrument concept evolved in the 80's time period, it will reflect the technology that was available during that time. With some of the 90's technology, selected components could be changed or updated and this will be discussed in a later portion of this presentation. The instrument design was also affected by the changing environmental concerns and issues at EPA in the 80's. The changing emphasis on water quality and soil analysis capabilities varied sufficiently, that the instrument is equally adapt in its capacity to handle either type of sample.

The unit as presently configured consists of four modules: 1) Water Sample Module, 2) Portable Analyzer Module, 3) Electronics Module and 4) Computer Module.

Water Sample Module

The water sample module is a unit designed by Martin Marietta to accept known volume water samples that have had a precipitant (Dibenzyldithiocarbomate) and a buffer (Potassium Hydrogen Phthalate) added and will perform the filtration process by depositing the precipitate on a membrane filter that is housed for ease of handling in a 35mm slide mount holder. The analyzer module will fit onto the water module and once the filtration step is complete (as indicated by filtration complete light), the operator has only to slide the 35mm holder from the filtration position to the analyzer position to initiate sample analysis.

Portable Analyzer Module

The portable analyzer module or sensor head is a combination of commercially procured instruments that were modified and incorporated in an enclosure designed by Martin Marietta. The detector is a Si(Li) solid state detector cooled by liquid nitrogen from a reservoir (dewar) that has sufficient capacity for 8-12 hours of operation. When not being operated in the portable mode, the dewar is attached by hose to a larger liquid nitrogen dewar and is automatically refilled when the liquid nitrogen is depleted. This detector and dewar system was procured from PGT, Inc. Due to the high elemental sensitivities needed by EPA, it was deemed necessary to go to the high resolution solid state detector rather than use the proportional counter tube type detector. Likewise, it was necessary to eliminate the use of radioactive isotopes as the X-ray source and go to a miniaturized X-ray tube for both the safety aspects as well as the need for the high intensity fluxes obtainable from a tube source. A 30 Kilovolt, molybdenum target, X-ray tube was built for this unit by X-Tech, Inc. and included as a part of the analyzer module. The high voltage bias and electronics power is supplied from an array of lead-zinc "Gel-cell" batteries located in the back section of the analyzer module.

Electronics Module

The electronics module is the pulse height analyzer, used to accumulate the energy pulses from the detector into an energy versus counts spectrum. Rather than attempting an extensive modification of the electronics used in the portable unit for the Bureau of Mines, a commercially available unit, the Canberra Series 10 Multi-channel Analyzer, was chosen instead which required only minor modification to interface with the analyzer and computer modules. It is capable of storing up to 16 spectra before transfer to computer storage is required. The rechargeable NiCad batteries power the unit and also provide detector bias and detector electronics power.

Computer Module

The computer module is used to accept and store the spectra received from the electronics module and to convert the spectral peaks to quantitative concentration values. The 80's saw considerable changes and increasing capabilities in small portable computers and as a result our original choice of the only mini-computer available at that time, the HP-85, rapidly became obsolete and so for our field tests, we switched to a Grid Case 2 portable unit. This too is rapidly on its way to being replaced with more powerful units, but the point is that our software as well as comparable commercial versions, will all work satisfactorily on 286 or higher number CPU machines.

The combination of the four modules comprise what we have designated as the "EMPAX" instrument (EMPAX being the acronym for Environmental Monitoring with Portable Analysis by X-Ray). The EMPAX instrument has been issued Patent No. 5014287.

FIELD DEMONSTRATION TEST

Two prototype units were built by Martin Marietta, one of which was delivered to EPA, Las Vegas Laboratories in Nevada and the other to NASA, Langley Research Center in Virginia. Before delivery, both units were involved in extensive field testing. To illustrate the potential usage of these units, the field trip to a Superfund site in Aspen, CO, conducted in August 1988 will be described. The site was chosen for being in driving distance to the Martin Marietta facilities in Denver, CO, and for having been already characterized for toxic pollutants which were chiefly mine tailings from operation of the mines in Smuggler Mountain. Working from dawn to dust at the site, the combined team of NASA, Martin Marietta and EPA personnel collected over 120 spectra at which time all the instruments and personnel needed regeneration. A normal survey of a site such as this one, involves the analysis of many samples in a certified laboratory, would take many months to obtain analysis results and would cost up to $100,000. The EMPAX instrument, in a few days, could also perform the site survey, would provide in-site analysis results and the total instrument fabrication cost is estimated at about $80,000. Thus, the instrument is very cost effective compared to standard analysis costs.

Water samples were also available at this site and were taken from the nearby outcrop stream. The analysis results surprised us with very high Z peaks that turned out to be Uranium. Since the water percolated through the abandoned and flooded old mine shafts, by hindsight, the presence of Uranium is not too unusual but demonstrates that XRFS because of its elemental scanning ability, will routinely detect the presence of unusual elements. Other analysis techniques such as Atomic Absorption or Emission Spectroscopy (ICP) require the preselection of elements of interest and this would miss the presence of elements that may also be of interest.

Comparison of the XRFS analysis to that performed by standard laboratory procedures as stated in the EPA evaluation report - "Precision and accuracy of the in-site measurements were within ±10% of the true value when compared to the samples analyzed in the laboratory." These results are considered outstanding by all parties concerned and exceed expectations for the analytical capabilities of the EMPAX in most situations.

POTENTIAL DESIGN CHANGES

The prototype instrument design was preset several years ago and with the continuing advances in the field of XRFS instrumentation, there are a number of changes that could be made to EMPAX to enhance its capabilities and commercial applications.

Electronic Module

In many of the commercial laboratory XRFS, the function of the PHA has been incorporated on a computer circuit board so as to use the computer terminal and keyboard functions as the PHA readout and controls. With the newer laptop computers being able to add full size boards, it is quite possible to combine the functions of the Canberra Series 10 Multichannel Analyzer into the Grid Case type computer and thereby eliminate one module entirely. The power supply functions of the PHA could then be transferred to the analyzer module.

Water Sample Module

The present design uses a membrane filter to collect the precipitate and thus achieve up to a 100 to 1 increase in concentration of the elements to be analyzed. With the advent of new ion exchange type membranes, it is possible to have the membrane filter act as the concentrator thus eliminating a time consuming filtration step. Since the ion exchange membrane can also act as a filter, it can also serve to collect the precipitate while concentrating the cations that do not react with the precipitant. By analyzing both the front and backside of the membrane filter, one can increase the number of cations that can be analyzed.

Analyzer Module

When initially designed, the portable liquid nitrogen cooled detector was a major advance over the use of proportional counter tubes. Now there are several commercially available units but the continual need of liquid nitrogen as a coolant is an impediment that could be rectified by changing to a thermoelectrically cooled detector. There are commercial available XRFS systems that use this means of cooling but power consumption is in order of 30 to 80 watts. The literature and experimental work by Martin Marietta has shown this power consumption can be reduced to 12 watts or lower which is within the ability of using batteries as the power supply. This change would eliminate the problem of obtaining or carrying liquid nitrogen to remote sites.

The prototype instrument lack of sensitivity to Cd, Sb and Ag is due to the choice of using Mo as the X-ray tube target source. The L line energies of these elements are obscured by the Argon present in the atmosphere and the K lines energies are too high to be excited by the Mo X-ray source. A possible simple means to enhance the sensitivity to these elements is to use some of the gaseous nitrogen from the boil off of the liquid nitrogen coolant and have it act as a purge over the sample to be analyzed. A more effective but more complex solution is to be able to selectively change the excitation source energy. As part of this project, a higher voltage (50 Kv) miniaturized X-ray tube was devised that provided dual energy outputs through the use of either a composite single target or a dual target source. This development came too late to include in the prototype instruments but have since become commercially available.

COMMERCIALIZATION

The prototype EMPAX instruments were built mainly to demonstrate feasibility and be used for field evaluation studies. During the design phase, consideration was made to make fabrication as simple as possible by using commercially available components, however modification and redesign is still needed if EMPAX is to be commercially marketed. As currently designed, the EMPAX instrument will meet most but not all of the FDA requirements for X-ray sources. Thus, some refinements plus any of the aforementioned enhancements must be made before this instrument could become a marketable product.

There is more emphasis today on the use of XRFS for environment monitoring and has become a recommended procedure by EPA. It is common now to use laboratory XRFS in vans for on-site analysis but the EMPAX instrument has the additional capability of performing in-situ analysis, a major advantage over sample removal and then perform the analysis.

Element	Line	Energy (keV)	Water Samples MDL, ppb*	Soil Samples MDL. ppm
Cr	Ka	5.414	100	1000
Ni	Ka	7.477	20	300
Cu	Ka	8.047	20	250
Zn	Ka	8.638	10	200
As	Ka	10.543	10	150
Se	Ka	11.221	10	140
Ag	Ka	22.162	200	>1000
Cd	La	3.133	ND	ND
Sb	La	3.605	ND	ND
Ba	La	4.467	200	>1000
Hg	Lb	11.823	20	80
Tl	Lb	12.210	30	75
Pb	Lb	12.610	20	70

ND = Not Detectable
*Assumes 100 ml sample volume containing single element only
ppm = parts per million ppb = parts per billion

Table 1. Mininum Detection Limits (MDL) for Priority Elements

Module	Size (in)	Weight (lb)	Power
Water Sample	18x18x10	40	AC
Portable Analyzer	22.5x11x12.5	34	4-Gel Cell Batt.
Electronics	4.5x9x11	12	5-NiCd Batt.
Computer	15x11x2.5	12	Rechargeable Batt.

Detector - LN2 cooled Si(Li)
X-ray Source - 30 Kv - Mo target - 0.2 ma
PHA - 4096 channels
0-600 volts bias power

Water Sample Module - Martin Marietta Design
Portable Analyzer Module - PGT Detector
- X-Tech X-ray Tube
- Martin Marietta Design
Electronics Module - Canberra Series 10 PHA
Computer Module - Grid Case 2 Portable Computer

Precipitant - Dibenzyldithiocarbamate
Filter Membrane - Rainin Nylon - 0.45 um pore size

Patent number - 5014287
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- Technology Utilization Office (804) 864-2482
EPA Las Vegas Contact - Bill Engelmann (702) 798-2664

Table 2. EMPAX instrument information

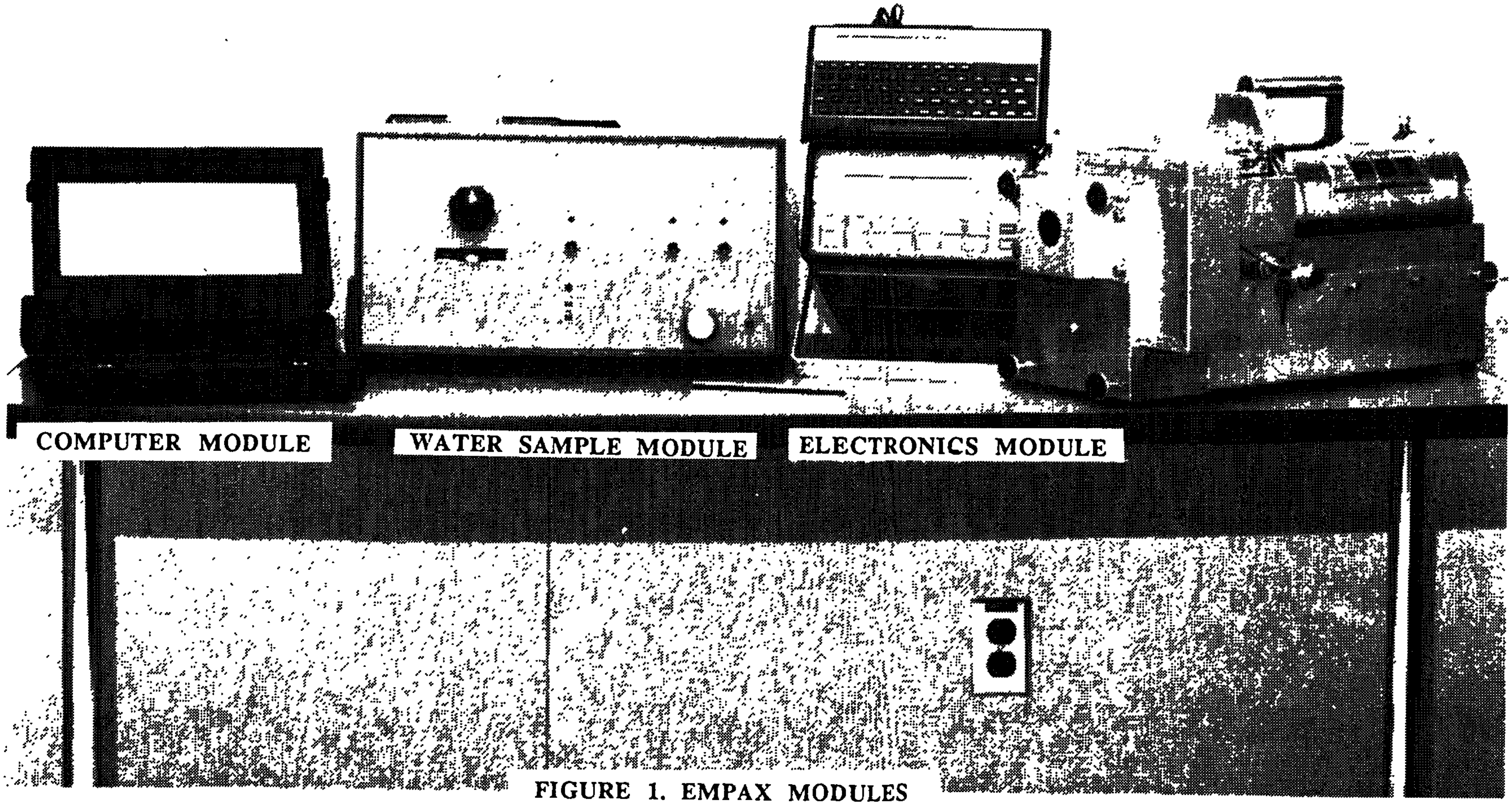

FIGURE 1. EMPAX MODULES

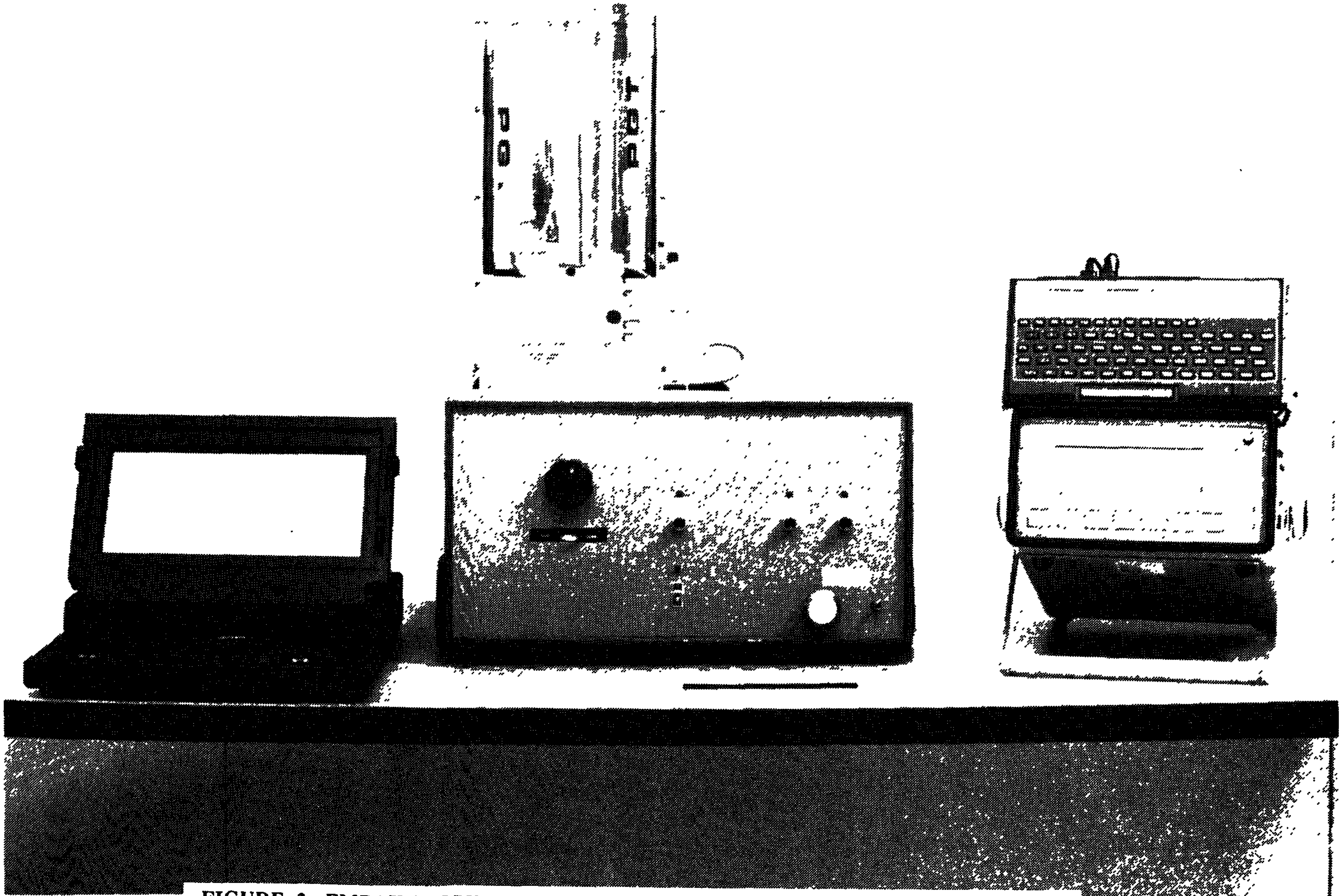

FIGURE 2. EMPAX MODULES WITH ANALYZER IN WATER SAMPLE MODULE

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FIGURE 3. EMPAX INSTRUMENT BEING USED AT CONTAMINATED SITE

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