

Low Cost Compact X-Ray Fluorescence Analyzer for On-Site Measurements of Single Elements in Source Emissions

L. S. BIRKS AND J. V. GILFRICH

*X-Ray Optics Branch
Material Sciences Division*

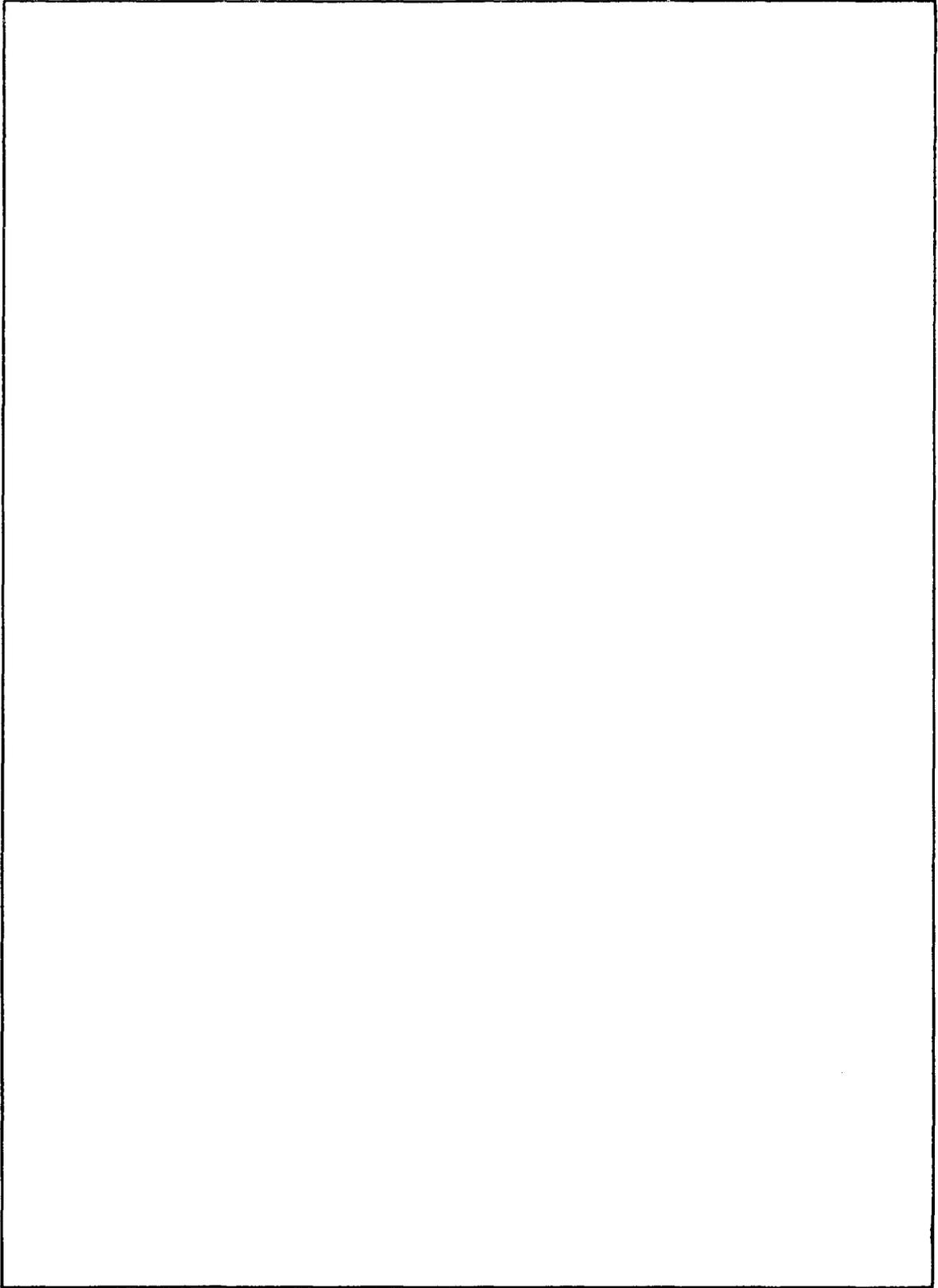
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INTRODUCTION

Fossil-fueled power plants, incinerators, and other sources emit substantial quantities of airborne particulate matter containing various amounts of such elements as Pb, Hg, Cd, As, Ni, V, Cr, Se, Mn, Cu and Sb that are of concern as actual or potential hazardous pollutants. An effective and economical means for on-site monitoring of emissions of these elements would be of considerable help in developing control strategy. The technique should be simple, rapid and have limits of detection adequate to analyze fairly short-time collections with an acceptable accuracy. The necessary equipment should be inexpensive so that even small operators could afford the capital expenditure.

X-ray fluorescence had already been demonstrated to be a valuable analytical tool for the measurement of the elemental composition of particulate pollution. (1-12) In view of this fact, the U. S. Environmental Protection Agency (EPA) requested the Naval Research Laboratory (NRL) to suggest a commercial x-ray analysis system to perform the monitor function, or to design and build an instrument specifically suited to this application.

COMMERCIAL INSTRUMENTS

The problem of evaluating low-cost x-ray instrumentation is complicated by the degree of sophistication which has been introduced by the x-ray manufacturers. The cost per sample has been reduced using this expensive equipment for those situations where the sample load is high enough to take full advantage of the automated instruments. However, the capital expenditure is impossible to justify for any industry which needs to analyze only a few samples.

Fortunately, there are several inexpensive x-ray analyzers commercially available and our first step was to examine their capabilities using a set of criteria agreed upon between the authors and the EPA project officer. It was felt that a reasonable target cost for the instrument was \$5000; it should have a 100 second detection limit of about $1 \mu\text{g}/\text{cm}^2$ for a single element (as particulate material deposited on a

thin substrate); it should be capable of measuring any one of a wide variety of elements with a resolution adequate to minimize interferences; it should be simple to use, compact and able to operate from a conventional 110 volt, 60 Hertz A.C. branch circuit. The types of instruments considered and the factors involved in evaluating them are listed in Table I.

TABLE I. PROPERTIES OF COMMERCIAL LOW COST X-RAY ANALYZERS

Type of Instrument	Scint. or Prop. Det. W Filters	Solid State Det. -Isotope	Solid State Det. -X-Ray Tube	Crystal Spectrometer
Cost	~\$5000	~\$8000	~\$15000	~\$10000
Weight	20 lbs	100 lbs	285 lbs	125 lbs
Resolution	Varies W each filter pair used. Typically 500 eV	180 eV @ 4 keV 200 eV @ 6 keV 220 eV @ 10 keV 270 eV @ 20 keV	180 eV @ 4 keV 200 eV @ 6 keV 220 eV @ 10 keV 270 eV @ 20 keV	25 eV @ 4 keV 68 eV @ 6 keV 143 eV @ 10 keV 650 eV @ 20 keV
100 Second Det. Limits	Few to Tens of $\mu\text{g}/\text{cm}^2$	$< 1 \mu\text{g}/\text{cm}^2$	$< 0.5 \mu\text{g}/\text{cm}^2$	$< 1 \mu\text{g}/\text{cm}^2$
Special Requirements	Need to examine each element to determine if approp. filters available.	Liq. N_2 (can have 28 day holding time)	Liq. N_2 (can have 28 day holding time)	None

As can be seen from Table I, none of the commercial instruments satisfy all the criteria. The first instrument is the only one which satisfies the cost criterion and is the only one which does not meet the detection limit requirements. The most discouraging observation from the table is the poor energy resolution of all of these particular systems. The lack of good energy resolution results in significant interferences which only can be overcome for the solid-state detector instruments by computer processing of the data (one of the ways in which the modern equipment has become sophisticated and expensive); the instruments using filters are simply not suited to any analysis situation involving such interferences. The particular crystal spectrometer listed used a low-power x-ray tube and inefficient geometry which made it necessary to sacrifice resolution for intensity. In general, however, the resolution of a crystal spectrometer can be considerably better than that listed in the table and suggested that such an instrument should be designed and constructed specifically for the problem at hand.

INSTRUMENT DESIGN

It was not the intent of the effort reported here to perform research in the area of crystal spectrometer design. Rather the instrument would use those state-of-the-art components which were commercially available and we would only custom-make those parts which were unique.

The Interagency Agreement between NRL and EPA specified the construction of a bread-board model but it was recognized early that a prototype would be much more useful. The complexity introduced by a vacuum system seemed unnecessary for this prototype and therefore the instrument would be limited to measuring those elements whose characteristic x-rays are not attenuated significantly in an air path.

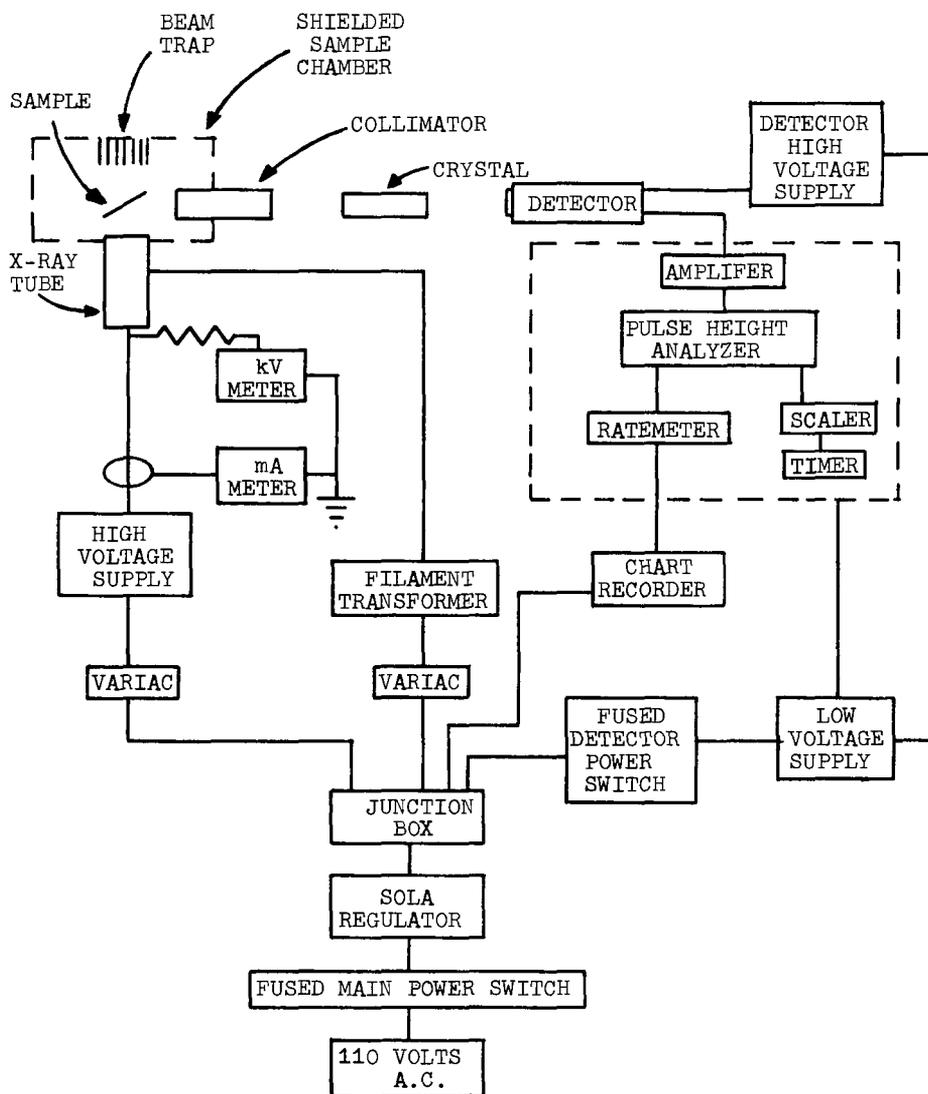


Figure 1. Block diagram of the Compact X-Ray Analyzer.

Figure 1 is a block diagram of the complete x-ray analysis system and Table II lists the commercial components and their cost, as well as the parts fabricated at NRL with the best estimate (probably good to 10 or 20%) of the cost to produce the latter. Assembly and testing of the equipment could be easily accomplished for an additional thousand

dollars, although a considerably larger amount was spent on the prototype to insure that the approach used was the most appropriate.

TABLE II
COMPONENTS FOR COMPACT X-RAY ANALYZER
PURCHASED COMMERCIALY

	<u>Manufacturer and Model No.</u>	<u>Cost</u>
Regulator	Sola 23-22-150	\$ 100
X-Ray Tube H. V. Supply	Universal-Voltronics BPE-40-4	415
X-Ray Tube	Machlett EG-50 HW	1050
"005 x 4" Collimator	Philips 19011200	255
Scintillation Detector	Harshaw SHG	310
Detector H. V. Supply	Venus Scientific K-15	150
Recorder	Rustrak 288	197
Electronics Power Supply	Sorensen MMD-12.120	96
<u>FABRICATED AT NRL</u>		
Crystal (LiF)	Cleaved, abraded and etched, from NRL stock	\$ ~50
Filament Supply	6.3 VCT Transformer, 1.5 Amp Variac and miscellaneous small parts	~25
X-Ray Tube Housing and Sample Chamber	Manufactured in NRL Shops: materials and labor	~500
Spectrometer, incl. Crystal and Detector Mounts	Gears (\$36) + machine work in NRL Shops: Mat'ls and labor	~100
Counting Electronics: Amp., PHA, Ratemeter Scaler, Timer, etc.	Some circuitry designed in NRL Electronic Shop, other circuitry standard: Mat'ls and labor	~500
Miscellaneous Cables Connectors and Electronics Comp.		~25
Cabinet to house components fabricated at NRL		~50
TOTAL		<u>\$3823</u>

The Sola regulator was used to stabilize the line voltage. The Universal-Voltronics high voltage supply was chosen largely on the basis of cost and size. Although a 50 kV supply would have been preferable in order to excite the heavier elements, Universal Voltronics had not built this power supply for more than 30 kV; therefore they were only willing to upgrade it to 40 kV, which we considered acceptable. The Machlett EG series x-ray tube was the only low-powered tube readily available; it was purchased with a tungsten target for efficient excitation over a wide atomic number range and with an unnecessarily

thin window (^{11}Be) because that particular model was in stock for rapid delivery. This x-ray tube is located in an oil-filled housing which, together with the specimen chamber, was fabricated at NRL. The tube housing is air cooled and contains a resistor stack by which the voltage applied to the tube is monitored. The specimen chamber contains a sample changing mechanism, the beam trap to prevent scattering of the primary beam which is transmitted through the sample, and the collimator. The x-ray tube current is controlled by the NRL-built filament supply. Both the x-ray tube housing and the specimen chamber were lined with lead to provide radiation protection.

The spectrometer, consisting of the crystal and detector and the θ - 2θ coupling between them by means of a planetary gear arrangement, is shown in Figure 2. The Harshaw SHG scintillation detector has a very good reputation with regard to its energy resolution and low noise. The detector high voltage supply, the low voltage power supply for the electronics package, and the recorder were commercial units; the rest of the counting electronics were designed and built at NRL, making use of modern conventional circuitry. Figures 3 through 5 are photographs of the completed instrument.

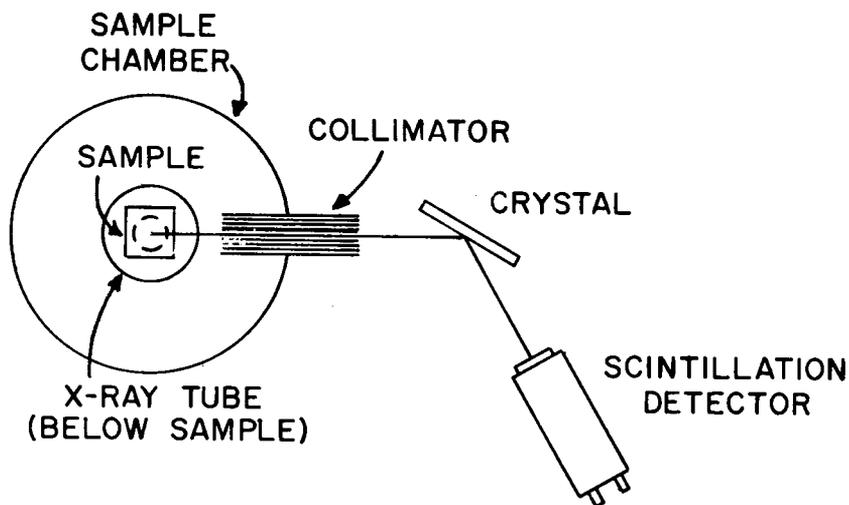


Figure 2. Plan view of spectrometer.

The operation of this prototype is identical with that of any wavelength dispersive x-ray fluorescence analyzer with which it is assumed the reader is familiar. The spectrometer is manual and must be set by hand for detecting the x-rays of interest; the crystal is coupled to the detector and automatically set at the diffracting angle. The intensity can be read on the scaler, ratemeter or strip-chart recorder.



Figure 5. Analyst inserting sample into instrument (preliminary front panel).

RESULTS

Sensitivity and Detection Limits

One of the parameters considered important in defining the usefulness of the compact x-ray analyzer described here is the detection limit for various elements. The original criterion was that the 100 second detection limit should be $1 \mu\text{g}/\text{cm}^2$ or better for the elements within its wavelength range. Measurements of the sensitivity $[(c/100 \text{ s})/(\mu\text{g}/\text{cm}^2)]$ and the detection limits ($\mu\text{g}/\text{cm}^2$) were made using single element standards of solutions deposited on filter paper.⁽¹⁾ The results of these measurements are listed in Table III and the detection limits are shown as a function of atomic number in Figure 6. It can be seen that the $1 \mu\text{g}/\text{cm}^2$ criterion is satisfied for all elements tested with the exception of Cd which is $1.2 \mu\text{g}/\text{cm}^2$. Many of the elements demonstrate detection limits significantly better, the best being Zn at $0.1 \mu\text{g}/\text{cm}^2$.

TABLE III
SENSITIVITY AND DETECTION LIMITS*

Element	X-Ray Line	Sensitivity [(c/100 s)/(μg/cm ²)]	BGD (c/100 s)	3σ D. L. (μg/cm ²)
V	Kα	245	1429	0.46
Fe	Kα	1249	3659	0.15
Cu	Kα	1582	7974	0.17
Zn	Kα	2111	5424	0.10
Br	Kα	1160	7009	0.22
Mo	Kα	596	6255	0.40
Cd	Kα	98	1504	1.2
W	Lα	587	34586 [†]	0.95
Pb	Lα	714	7993	0.38
U	Lα	553	6480	0.44

* 100 second measurements with W target Machlett EG-50 x-ray tube operated at 40 kV, 2 mA.

[†]High background due to scattered primary W L lines.

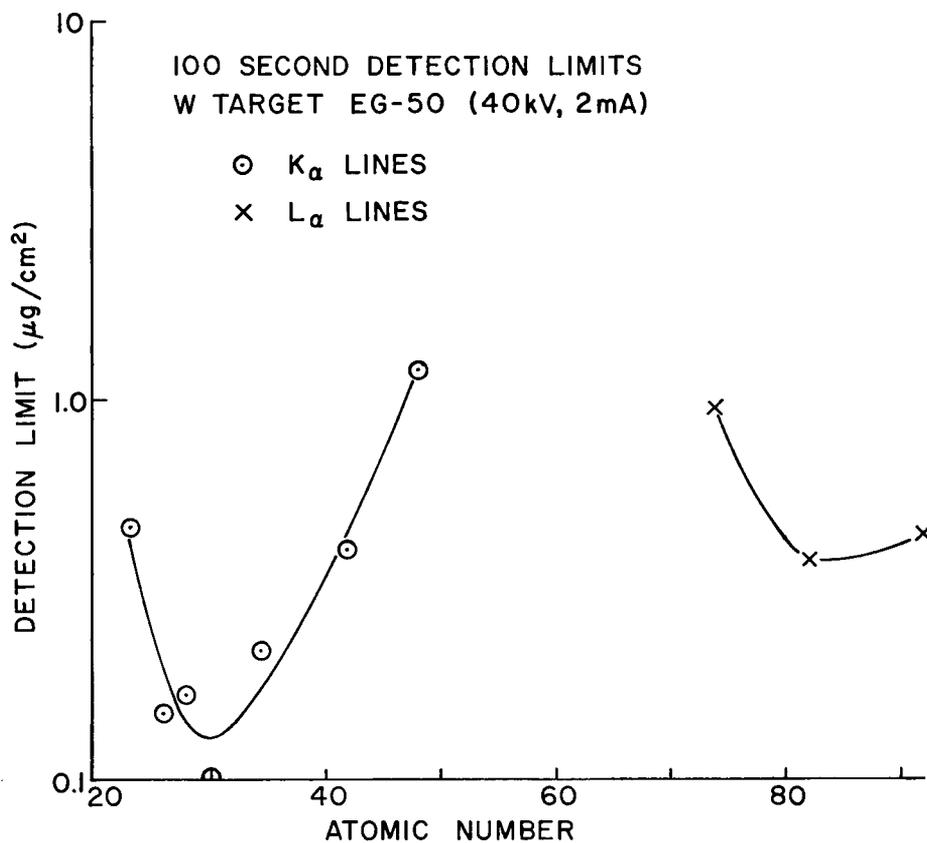


Figure 6. Detection limits as a function of atomic number.

Sample Measurement

The instrument was further tested by analyzing some auto exhaust samples provided by EPA. During these measurements, some difficulty was experienced due to a faulty component in the detector high-voltage supply. Unfortunately, these samples had also been analyzed in the standard laboratory spectrometer and had received enough radiation exposure that they were very brittle. While attempting to remeasure these samples in the single element analyzer they deteriorated and only a few of the samples could be analyzed for some of the elements. The results of these few determinations are shown in Table IV. The "less than" value of $0.13 \mu\text{g}/\text{cm}^2$ listed for Br in sample 07 is not inconsistent with the detection limits shown in Table III. Sample 07 was collected on a Nuclepore filter which, because it is significantly thinner than Millipore or Whatman filters, contributes a smaller scattered background. This leads to better detection limits than those listed in Table III ($0.13 \mu\text{g}/\text{cm}^2$ for Br compared to $0.22 \mu\text{g}/\text{cm}^2$ in the Table).

TABLE IV
COMPARISON OF COMPACT X-RAY ANALYZER
RESULTS WITH THOSE OBTAINED USING
A STANDARD LABORATORY X-RAY ANALYZER

<u>Sample No.</u>	<u>Concentration, $\mu\text{g}/\text{cm}^2$</u>			
	<u>05</u>	<u>06</u>	<u>07</u>	<u>08</u>
<u>Pb</u>				
PW 1410*	3.6	0.45		
CXA	5.2	0.50		
<u>Br</u>				
PW 1410	1.1		0.07	
CXA	1.1		<0.13 [†]	0.28
<u>Fe</u>				
PW 1410		32		4.7
CXA		34		5.2

*PW 1410 is the standard laboratory instrument.
CXA is the compact x-ray analyzer.

[†]"Less than" value indicates the 3σ , 100 s. detection limit.

Field Test

Since the instrument was designed to be operated conveniently on the site of an emission source, the final test before transferring it to the EPA was conducted in the field. Arrangements were made by the EPA to collect samples of particulate material from one of the stacks

at the River Bend Plant of the Duke Power Company in Charlotte, North Carolina, and to measure several elements at that location using the compact x-ray analyzer. The instrument was transported from NRL to the EPA Environmental Sciences Research Laboratory in Research Triangle Park, North Carolina by EPA vehicle. At that location, the analyzer was set up and put into operation to insure that it had not been damaged during transport. Some minor malfunctions were remedied and the analyzer was made ready for the trip to Charlotte, again in an EPA truck. The original intention was to make the measurements in the EPA instrument shack located on the roof of the plant, immediately adjacent to the stack fitted with sampling ports. However, it was apparent that conveying the instrument to the roof would not demonstrate anything that could not be shown as well by setting it up in the plant laboratory and there was some chance of damage in attempting to navigate the tortuous path to the roof. As at the EPA laboratory, the analyzer was set up and put into operation. Sample deposits on Millipore filters were taken from the stack and measured for six elements using "solution on filter paper" standards prepared at NRL. The results are shown in Table V. At the conclusion of this operation, the analyzer was transported back to the Environmental Sciences Research Laboratory.

TABLE V
COMPACT X-RAY ANALYZER RESULTS
ON POWER PLANT PARTICULATE SAMPLES

	Concentration ($\mu\text{g}/\text{cm}^2$)	
	<u>Sample X-2</u>	<u>Sample X-5</u>
Mn	0.4	0.5
Fe	31	33
Ni	0.3	0.5
Zn	$<0.8^*$	7.1
Hg	5.7	2.7
Pb	4.7	5.1

* Zn was not detectable on sample X-2. The anomalously high 100 sec. detection limit ($0.8 \mu\text{g}/\text{cm}^2$) was caused by the high Zn content of the "o-ring" used to clamp the filter in the sample holder.

SUMMARY

The design, construction and testing of the instrument described in this report demonstrates that a compact, low powered, relatively inexpensive, wavelength dispersion x-ray analyzer can be produced using state-of-the-art components. It is capable of measuring elemental composition of the particulate material collected from emission

sources (or from ambient air, for that matter) with 100 second 3σ detection limits ranging from 0.1 to 1 $\mu\text{g}/\text{cm}^2$ for elements which can be analyzed in an air path instrument. The cost of the components used to fabricate such an instrument was well below \$5000 and we estimate that, even in the present (1975) economy, if produced in sufficient quantity, similar instruments should be commercially marketable for not more than \$10,000.

If an instrument of this type were to be commercially produced as a "single element" analyzer, this would enable the device to be customized, e.g., the use of a (220) LiF crystal and 50 kV power supply for measurements of the K lines of elements from Ru to Cd; the amplifier gain, PHA settings and Bragg angle fixed rather than adjustable; a selection made of digital or analog readout depending on the application, and the sample chamber specifically adapted to the samples being measured. Thus the instrument might have only two controls, "on-off" and "read", for simplicity of operation. Conversely, the degree of complexity could be increased to make the analyzer more versatile (but unfortunately more expensive) by providing a motor drive for the spectrometer, enclosing the specimen chamber and spectrometer in a vacuum housing, installing a crystal changer and a thin-window proportional detector, etc.

Several of the x-ray equipment manufacturers have seen this device and discussed the design parameters involved in the production of an inexpensive instrument of this type. They all expressed interest and some of them are currently considering the possibility of making such an instrument commercially.

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REFERENCES

1. "Development of X-Ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions," L. S. Birks, J. V. Gilfrich and P. G. Burkhalter, EPA-R2-72-063, Oct. 1972.
2. "Development of X-Ray Fluorescence Spectroscopy for Elemental Analysis of Particulate Matter in the Atmosphere and in Source Emissions. Phase II: Evaluation of Commercial Multiple Crystal Spectrometer Instruments," L. S. Birks and J. V. Gilfrich, NRL Report 7617, June 1973.

3. J. V. Gilfrich, P. G. Burkhalter and L. S. Birks, *Anal. Chem.* 45, 2002 (1973).
4. F. S. Goulding and J. M. Jaklevic, Lawrence Berkeley Laboratory, UCRL-20625, May 1971.
5. H. R. Bowman, J. G. Conway and F. Asaro, *Environ. Sci. Technol.* 6, 558 (1972).
6. T. R. Dittrich and C. R. Cothorn, *J. Air Pollut. Contr. Ass.* 21, 716 (1971).
7. T. B. Johansson, R. Akselsson and S. A. E. Johansson, Lund Institute of Technology, LUMP 7109, Aug. 1971.
8. R. L. Watson, J. R. Sjurseth and R. W. Howard, *Nucl. Instrum. Methods* 93, 69 (1971).
9. J. S. Cooper, *Nucl. Instrum. Methods* 106, 525 (1973).
10. J. Leroux and M. Mahmud, *J. Air Pollut. Contr. Ass.* 20, 402 (1970).
11. P. Greenfelt, A. Akerstrom and C. Grosset, *Atmos. Environ.* 5, 1 (1971).
12. C. L. Luke, T. Y. Kometani, J. E. Kessler, T. C. Loomis, J. L. Bove and B. Nathanson, *Environ Sci. Technol.* 6, 1105 (1972).