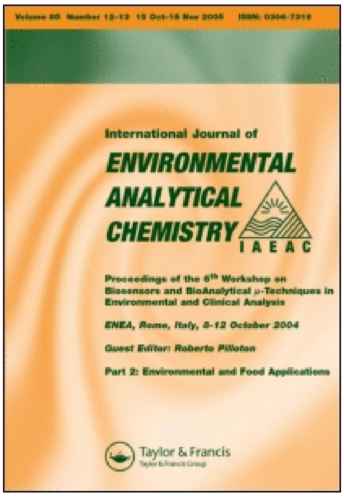
This article was downloaded by:
On: *18 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Impact of Personal Computers and New Instrumentation on Environmental Applications of X-ray Fluorescence

D. E. Leyden[a]; A. R. Harding[a]; A. Rachetti[b]; W. Wegscheider[b]
[a] Colorado State University, Fort Collins, CO, U.S.A [b] Technische Universität Graz, Graz, Austria

To cite this Article Leyden, D. E. , Harding, A. R. , Rachetti, A. and Wegscheider, W.(1986) 'Impact of Personal Computers and New Instrumentation on Environmental Applications of X-ray Fluorescence', International Journal of Environmental Analytical Chemistry, 27: 1, 69 — 80

To link to this Article: DOI: 10.1080/03067318608078391

URL: http://dx.doi.org/10.1080/03067318608078391

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem., 1986, Vol. 27, pp. 69–80
0306-7319/86/2702-0069 $18.50/0
© 1986 Gordon and Breach, Science Publishers, Inc.
Printed in Great Britain

Downloaded At: 19:48 18 January 2011

Impact of Personal Computers and New Instrumentation on Environmental Applications of X-ray Fluorescence†

D. E. LEYDEN and A. R. HARDING
Colorado State University, Fort Collins, CO, 80523, U.S.A.

and

A. RACHETTI and W. WEGSCHEIDER
Technische Universität Graz, A-8010 Graz, Austria

(*Received March 20, 1986*)

X-ray spectrometry is a powerful quantitative tool with many applications to analysis of environmentally related samples. Until recently, computer programs used for X-ray data analysis and treatment required mainframe or expensive minicomputers. Microcomputer systems now supplied with the instrumentation or generally available in the laboratory are equipped with the necessary memory and speed to permit execution of large programs for matrix corrections or those known as fundamental parameter programs. These computers can serve equally well as the data acquisition and instrumental control system. Examples of results obtained using such systems are presented.

KEY WORDS: X-ray spectrometry, XRF, microcomputers, fundamental parameters, elemental determinations.

---

†Presented at the 16th Symposium on the Analytical Chemistry of Pollutants, Lausanne, Switzerland, March 17–19, 1986.

INTRODUCTION

There are many reports of the application of X-ray spectrometry to environmental analysis. It is not possible to present a literature review here, but many general references,[1] reports of applications to investigations of air pollution,[2] and applications to the determination of elements in water[3] are available. These reports may vary somewhat in the conclusions, yet it seems clear that using sophisticated equipment such as PIXE,[4] and routine commercial spectrometers,[4] the lower limits of detection are a few ng/cm^2 to a few hundreds of ng/cm^2 for thin film samples, and a few μg/g for bulk samples. The exact detection limits depend upon the analyte element, the type and configuration of the instrumentation, and the acquisition time allotted. Nonetheless, the values are high for the usual requirement of environmental analyses. As a result, some type of enrichment or preconcentration technique is often required when X-ray spectrometry is employed in environmental determinations. A relatively new application of an optical design known as total reflection X-ray fluorescence (TRXRF)[5] is demonstrating absolute detection limits of a few nanograms and may offer some additional applications of X-ray spectrometry for environmental analysis.

Downloaded At: 19:48 18 January 2011

Other than TRXRF, there has been little development in practical X-ray spectrometric instrumentation in the past decade of significant value to environmental determinations. However, a recent general trend toward the application of microcomputers in conjuction with X-ray spectrometry has offered some interesting possibilities. A brief explanation of the significance of this trend is appropriate.

The intensities of X-ray emission lines from elements in a specimen are given by a rather simple relationship shown in Eq. (1).

$$I_L = I_0 \omega_A g_L \frac{r_A - 1}{r_A} \frac{d\Omega}{4\pi} \frac{C_A \mu_A(\lambda_{pri}) csc\phi}{\mu_M(\lambda_{pri}) csc\phi + \mu_M(\lambda_L) csc\psi} \tag{1}$$

Table I shows the definition of the terms in Eq. (1). Equation (1) is easily solved for the emission intensity of any element if all of the parameters are known, and if monochromatic source radiation is used. These two conditions are not easily met. First, there are no practical sources of true monochromatic x-radiation. Radioisotopes which decay with X-ray emission are possible solutions. Feasible

TABLE I
Definition of terms in Eq. 1

I_L	is the analyte line intensity.
I_0	is the intensity of the primary beam with effective wavelength λ_{pri}.
λ_{pri}	is the effective wavelength of the primary X-ray
λ_L	is the wavelength of the measured analyte line.
ω_A	is the fluorescent yield of analyte A.
g_L	is the fractional value of the measured analyte line L in its series.
r_A	is the absorption edge jump ratio of analyte A.
C_A	is the concentration of analyte A.
$\frac{d\Omega}{4\pi}$	is the fractional value of the fluorescent X-ray that is directed toward a detector.
$\mu_A(\lambda_{pri})$	is the mass absorption coefficient of analyte A for λ_{pri}.
$\mu_M(\lambda_{pri})$	is the mass absorption coefficient of the matrix for λ_{pri}.
$\mu_M(\lambda_L)$	is the mass absorption coefficient of the matrix for analyte line λ_L.
ϕ	is the incident angle of the primary beam.
ψ	is the takeoff angle of fluorescent beam.

Downloaded At: 19:48 18 January 2011

isotopes emit x-radiation at an energy above the absorption edge of the analyte element. Normally a single energy or widely separated energies are emitted. However, the radiation flux from sources safely used in a laboratory is so low that extensive analysis times are required. Secondary targets are another possibility. In this case, an X-ray tube is used to excite a pure element target which in turn emits the characteristic lines of the target element. Normally two or more lines of closely spaced energies are emitted. This approach is inefficient in power utilization. Because the excitation efficiency decreases significantly as the energy of the source X-ray becomes larger than the absorption edge of the analyte element, both radioisotopes and secondary targets have the disadvantage of a need for several isotopes or targets to cover a wide range of elements. By using filters between an X-ray tube and the specimen, the tube output may be conditioned to approximate monochromatic radiation if the characteristic lines of the tube target can be used. However, because often the continuum emission from the tube is utilized, even this approach is not always suitable. The result of these problems is that the specimen is normally excited by a continuum of x-radiation over a considerable energy range and including the characteristic emission lines of the X-ray tube. Equation (1) does not become more complicated, but more cumbersome because of the need to integrate the intensity components from the continuum X-ray source by numerical methods.

A further complication is that real samples are not single element materials. The effective mass absorption coefficients for the primary and emitted radiation will depend upon sample composition, which initially is not known. The sensitivity in counts per unit concentration will depend on the composition of the specimen. This problem is generally known as matrix effects and can be overcome by iterative or regression methods.

Finally, many samples are not infinitely thick. This means that the excitation radiation is not completely absorbed as it traverses the sample. In such cases, the emitted X-ray intensity will be dependent upon the mass of the sample, as well as the concentration of the analyte element. Sample to sample variations in mass must be compensated. Programs have been written to accomplish this task using the intensity of scattered source radiation to estimate the mass. The ratio of the coherent to incoherent scatter intensities may also be used to estimate the composition, or at least the X-ray absorption properties, of materials consisting mainly of low atomic numbered elements.

Downloaded At: 19:48 18 January 2011

Equation (1) offers a significant opportunity. If the instrumental geometric factors can be estimated, Eq. (1) permits the calculation of the sensitivity for all elements in a specimen if the various parameters are known. Computer programs to perform the above mentioned computations have been available for many years. The intensity of X-radiation emitted from an element in a specimen depends upon several factors shown in Eq. (1) including concentration of that element, the percentage of excited atoms of the element which emit an X-ray (fluorescence yield), the excitation efficiency, instrumentation geometry, absorption of source and emitted radiation by the matrix and others.[6] In principle, one may calculate the expected intensity for an X-ray emitted from a given element in a sample. In the case of instruments in which X-ray tube excitation is employed, the continuum emitted by the X-ray tube plays a role in the excitation. Therefore, the computation must model the tube output for the intensity distribution of the continuum emission, and to integrate the intensity emitted by elements in the sample over these excitation intensities at various energies.

One of the best known of these programs is NRLXRF which became available in 1978.[7] This program is written in FORTRAN and requires a mainframe computer. In 1980, NRLXRF was modified to execute on Digital Equipment Corporation (DEC) PDP/LSI-11 or VAX series computers using the RT-11 operating system.[8] This program was made available commercially as XRF-11 from Criss Software.[9] Although such computers as the PDP-11 are still used by some vendors of X-ray equipment, they are slow, memory limited, and relatively expensive. The cost of the computer hardware is especially high in comparison with the much less expensive "personal computers" which offer an order of magnitude more memory and acceptable execution speed.

In the past few years, the personal computer has had a substantial impact on the field of X-ray spectrometry. In the case of wavelength dispersive spectrometers (WDXRF), automation using personal computers and including data treatment software was established. One example is the package provided by Dapple Systems which includes a control interface for the spectrometer and data analysis software using an Apple IIe computer.[10] However, the introduction of the IBM PC family, including the XT and AT series with hard disk drive, has significantly opened the potential for use of these computers, in part because of the expanded memory capability to 512 kbytes and more of RAM, and support of a variety of computer languages. As a result, programs which only a few years ago required access to a large mainframe computer now can be executed on a relatively inexpensive personal computer.

Downloaded At: 19:48 18 January 2011

EXPERIMENTAL

Instrumentation

Two energy dispersive X-ray spectrometers were used. A Tracor Xray Inc., TX5000 equipped with a Rh X-ray tube and Rh filters was employed for the work done at Colorado State University. This instrument uses an IBM PC/AT for the data acquisition and control of the instrument. A menu selection of software permits a wide choice of correction and/or fundamental parameter programs to be selected. The fundamental parameter program is essentially a version of NRLXRF.[7] All software is written in the "C" language.

A Philips/EDAX EXAM VI spectrometer equipped with a W side window X-ray tube which irradiates a turret selected Ti, Zr or Sm secondary target was used for the work at the Technische Universität Graz. The system was calibrated with metal foils for the elements Al, Ti, Co, Ni, Cu, Zn, Nb, Mo, Sn, Ta, W, Au and Pb (Goodfellow Metals Ltd., Cambridge, UK) and with compounds deposited on Whatman 541 cellulose filters for the elements P, S, Cl, K, Ca, As, Br, Sr, Cd and Sb (Columbia Scientific Industries Corp., Austin, TX). The programs applied to the data taken from this instrument were written at the Technische Universität Graz. Although these programs were not executed on a microcomputer, they are easily adapted to such a computer.

Software used to extract intensities from the X-ray spectra were in both cases that supplied by the vendor.

Downloaded At: 19:48 18 January 2011

Sample preparation

Samples were fine powders which were pressed into pellets before analysis. If covers such as Mylar foil were used, spectra of these materials were subtracted prior to data analysis.

RESULTS AND DISCUSSION

The examples presented here are intended to show the potential of energy dispersive X-ray spectrometry as a tool for the quantitative determination of trace elements in a variety of samples with the use of no standards, or one standard similar to the unknown. Reasonable quantitative accuracy is possible without a set of matched standards. In the case of samples which are metal alloys, or oxides such as geologic materials, fundamental parameter programs work well because most of the information required to quantitatively describe the physical X-ray parameters are available from intensity data which is collected. However, in the case of biological or other organic material, much of the matrix does not exhibit detectable X-ray emission. In these cases, the use of scattered radiation as an additional source of information is required.

Downloaded At: 19:48 18 January 2011

Two examples will illustrate the potential of currently available programs for personal computers. Tracor X-ray Inc. introduced a version of NRLXRF called PCXRF which is written in "C" language for the IBM PC family.[11] This program is currently available as part of the instrument package for the TX5000 spectrometer. PCXRF is executed from a meanu by simply typing an "F" to select fundamental parameters. Table II shows results for trace element determination in NBS plant material standard reference material samples using PCXRF. For these determinations, three different excitation conditions were used to obtain the intensity data. NBS orchard leaves (SRM 1571) were used as the single standard. The nitrogen content of this SRM was fixed at the given value of 2.76%, and the remaining matrix composition was estimated as $C_6H_{12}O_5$ for the difference between the determined elements and 100% composition by weight. The difference composition is taken as typical carbohydrate composition of plant material. PCXRF has a limitation at present in that values must be entered in percent composition and the data field does not permit an adequate number of digits to enter values which are in the μg/g range with sufficient precision. This artificially limits the accuracy in the results. However, except for low atomic number elements which are very sensitive to matrix effects, and elements below about 50 μg/g, the agreement between certified and determined values is good in most cases. The conclusion is that with a commercial instrument using the vendor software and no exceptional sample preparation, one SRM standard can provide for determinations of trace elements in plant material with an accuracy of 3–20% for most elements. This is very encouraging for screening of a variety of environmental samples.

A second example is a program based on the work of Stephenson[12,13] known as CORSET which has been available for several years for large computer systems. This program has recently been converted to execute on the APPLE II computer equipped with a Z80 card and CP/M, and the IBM PC family, and is available for a modest cost.[14] Table III shows results for the use of CORSET on an IBM PC/AT for the determination of trace elements in the same plant materials shown in Table II. CORSET uses a less rigorous model for the X-ray tube output[12] than used in PCXRF. However, comparable relative errors are accomplished with either program depending on the number and quality of standards available. A set

Downloaded At: 19:48 18 January 2011

TABLE II

Results of the analysis of plant material using PXCRF (μg/g)

Element	NBS 1570 Spinach		NBS 1571[a] Orchard leaves		NBS 1572 Citrus leaves		NBS 1573 Tomato leaves		NBS 1575 Pine Needles	
	Certified	Found	Certified	Found	Certified	Found	Certified	Found	Certified	Found
Mn	16.5	16	9.0	6.0	2.3	1.0	23.8	18	67.5	60
Fe	55	43	30	28	9.0	9.0	69	51	20	19
Ni	0.6[b]	0.0	0.1	nd	—	nd	—	nd	3.5[b]	nd
Cu	—	—	1.2	1.0	1.6	1.0	1.1	1.0	0.3	1.0
Zn	5.0	5.0	2.5	4.0	2.9	3.0	6.6	7.0	—	9.0
As	—	—	1.0	2.0	—	nd	—	—	—	nd
Rb	1.2	1.0	1.0	1.0	0.5	1.0	1.6	2.0	1.2	1.0
Sr	8.7	9.0	3.7	4.0	10	11	4.5	6.0	—	nd
Pb	1.0	0.0	4.5	4.0	1.3	1.0	0.6	1.0	1.1	1.0

[a] A replicate specimen was prepared of the material used as the standard.

[b] Non-certified values.

Downloaded At: 19:48 18 January 2011

TABLE III

Results of the analysis of plant material using CORSET ($\mu g/g$)

	NBS 1570 Spinach		NBS 1571[a] Orchard leaves		NBS 1572 Citrus leaves		NBS 1573 Tomato leaves		NBS 1575 Pine needles	
Element	Certified	Found	Certified	Found	Certified	Found	Certified	Found	Certified	Found
Mn	16.5	16.9	9.0	7.0	2.3	1.4	23.8	18.3	67.5	77.1
Fe	55	46.1	30	32	9.0	9.9	69	49.6	20	24.6
Ni	0.6[b]	—	0.1	—	—	—	—	—	3.5[b]	—
Cu	—	1.0	1.2	1.2	1.6	1.2	1.1	0.9	0.3	1.0
Zn	5.0	5.0	2.5	3.7	2.9	2.9	6.62	5.5	—	10.2

[a] A replicate specimen was prepared of the material used as the standard.

[b] Non-certified values.

of benchmark tests for execution time were run on a variety of computers. Results range from 45 sec execution time for an IBM PC without an 8087 coprocessor, to less than 4 seconds for an IBM compatible NCR PC-8 (National Cash Register) equipped with an 80287 coprocessor. Both CORSET and PCXRF provide excellent capability to execute fundamental parameter programs for X-ray spectrometry using personal computers which are readily available at modest costs.

Many samples of environmental interest which are suitable for X-ray analysis consist mainly of a matrix of low atomic number elements which do not emit X-radiation which is detectable by the usual instrumentation. Therefore, estimates of the composition of the sample cannot be obtained from the measured X-ray intensities alone. The total composition of the specimen is required for fundamental parameters software to perform well. Relationships between the coherent and incoherent scatter of x-radiation from the sample provide an additional source of information which aids in the determination of the composition of the matrix when one or two low atomic number elements make up the major components.[15] Using this approach, a program was written to use the scatter from two secondary targets to estimate the low atomic number element composition of such materials.[16] Scatter from two targets was used to better describe the matrix composition. The only standardization was to collect intensities for a set of pure element foils, or elements in suitable compounds supported on a cellulose filter. The results obtained compare well with the certified values of the SRM's used as unknowns. Table IV shows results obtained using this program.

CONCLUSIONS

It is very apparent that X-ray spectrometry, like many other instrumental methods of analysis, will benefit greatly from the capabilities of the personal computer families. The hardware is more than capable of controlling the instrumentation and collecting the data. A few years ago the computational capabilities of these computers were limited. Now, that is greatly expanded as well, and

Downloaded At: 19:48 18 January 2011

TABLE IV

Trace element determination using no standards (μg/g)

Element	Aquatic plant		Aquatic moss		Bituminous coal	
	Certified	Found	Certified	Found	Certified	Found
Cr	532	496	532	469	34.4	15.7
Mn	1759	2120	3771	3709	28	nd
Fe	2380	2520	9303	8100	1.11%	1.09%
Ni	40	47	420	458	19.4	36.7
Cu	51.2	50.1	720	685	16.5	20.6
Zn	313	352	566	565	28	32
Br	20	18	22	17.5	41	55
Pb	63.8	71	64	67.1	12.4	8.9

Downloaded At: 19:48 18 January 2011

it is hard to imagine a computation associated with X-ray spectrometry that cannot be executed on a modern personal computer. The fact that quantitative trace analysis of a variety of sample types may be performed with an accuracy of approximately 10% or less in many cases without the use of standards has obvious implications for environmental monitoring. An important feature in the near future will be the networking capability of these computers so that results from an instrument may be transmitted rapidly and with minimal chance of error to a central data base which will gather information on each sample.

Acknowledgements

The work by DEL was supported in part by TRACOR XRAY INC., Mountain View, CA. The work by AR and WW was supported in part by a grant from the Fonds zur Förderung der wissenschaftlichen Forschung, Vienna, project P5200.

References

1. T. G. Dzubay, (Ed), *X-ray Fluorescence Analysis of Environmental Samples,* (Ann Arbor Science Publishers, 1977).
2. D. E. Leyden in H. Malissa, (Ed), *Analysis of Airborne Particles by Physical Methods,* (CRC Press, West Palm Beach, Fl, 1978), pp. 27–38.
3. D. E. Leyden in H. B. Mark Jr. and J. S. Mattson, (Eds), *Water Quality Measurement, The Modern Analytical Techniques,* (Marcel Dekker, Inc, 1981), pp. 271–306.

4. J. M. Jaklevic and R. L. Walter in T. G. Dzubay, (Ed), *X-ray Fluorescence Analysis of Environmental Samples,* (Ann Arbor Science Publishers, 1977), pp. 63–76.
5. R.-P. Stössel and A. Prange, *Anal. Chem.,* **57,** 2880 (1985).
6. E. P. Bertin, *Principles and Practices of X-ray Spectrometry,* (Plenum Publishing Co., New York, 1975), 2nd ed., p. 120.
7. J. W. Criss, L. S. Birks and J. V. Gilfrich, *Anal. Chem.* **50,** 33 (1978).
8. J. W. Criss, *Adv. X-ray Anal.* **23,** 93 (1980).
9. Criss Software, 12204 Blaketon St., Largo, MD, 20772, USA.
10. Dapple Systems, P.O. Box 2160, Sunnyvale, CA, 94087, USA.
11. Tractor X-ray Inc., 345 E. Middlefield Rd., Mountain View, CA, 94043, USA.
12. D. A. Stephenson, *Anal. Chem.* **43,** 934 (1971).
13. D. A. Stephenson, *Anal. Chem.* **43,** 1761 (1971).
14. Research Corporation/Research Software, 6840 E. Broadway Blvd., Tucson, AZ, 85710, USA.
15. K. K. Nielson, *Anal. Chem.* **49,** 641 (1977).
16. A. Rachetti and W. Wegscheider, *Anal. Chim. Acta,* in press (1986).

Downloaded At: 19:48 18 January 2011