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X-RAY FLUORESCENCE CAPABILITIES FOR URANIUM ORE ANALYSIS

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ABSTRACT

A rapid x-ray fluorescence (XRF) method for the quantitative analysis of uranium in ore and process samples is demonstrated. The method requires no uranium ore standards and provides a relative precision of $\pm 2.5\%$. Particle-size and self-absorption effects are evaluated along with current methods of excitation and detection for M, L, and K series uranium x-rays. Sensitivities and detection limits are comparable using either energy dispersive or wavelength dispersive analysis of uranium L x-rays, and wavelength dispersive analysis of uranium M x-rays for both thick and thin samples. The XRF methods are more sensitive than the analysis of uranium by ^{252}Cf neutron-induced γ -ray analysis or by direct photon analysis of uranium daughters.

INTRODUCTION

Increased demands for uranium have intensified exploration for new uranium ore deposits and evaluations of known low grade ores. Since both of these activities require relatively accurate and often rapid analyses for uranium, the capabilities of relevant analytical technology should be clearly understood.

This paper discusses uranium analysis in ores using a general purpose, multielement approach suitable for widely varying sample matrices without ore standards. It also considers parameters such as self absorption, particle size, packing fraction, and the excitation and detection methods for optimizing uranium determinations.

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT EY-76-C-06-1830

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The analytical capabilities of various x-ray fluorescence (XRF) methods are then compared with each other and with methods involving non-fluorescent photon analysis.

ANALYTICAL METHOD

Theory

Quantitative XRF analysis for uranium in geological materials has usually relied on standard reference materials which approximated the unknowns in composition, particle size and compaction. Our requirements for uranium analyses in a broad range of materials such as fuel samples, raw ores and low-level environmental samples suggested the need for a rapid, inexpensive analytical approach which did not involve matching standards for every sample type. We have therefore applied a general purpose multielement method previously developed for environmental sample analysis (1) to the determination of uranium.

The basis of the method is a computer code (2), SAP3, which approximately solves for all significant components in the sample matrix and then computes the appropriate self-absorption, enhancement and particle-size corrections for the individual sample. The code uses a dual library consisting of a list of heavy elements which are potentially measurable with the given instrument setup ($Z > 16$), and a list of light elements ($Z < 16$) which potentially define the remainder of the sample mass. Photoelectric and scattering cross sections, fluorescent yields, thin sample sensitivities and related parameters are also contained in the library. Quantities of the heavy elements are first approximated from their fluorescent peaks using thin sample sensitivities. Intensities of both coherent and incoherent scatter peaks resulting from the heavy elements are then computed, and the differences between the computed scatter peak intensities and those observed in the spectrum are attributed to light elements. The ratio and magnitudes of these intensity differences are used to identify and quantify the light elements which best approximate the remaining sample mass. Heavy element quantities are then corrected for self absorption, enhancement and particle-size effects using factors computed from the estimated heavy and light element concentrations. The corrected heavy element masses are then used to re-determine the light elements in an iterative fashion until convergence is achieved.

Experimental

Finely ground ore samples were mixed with an equal mass of cellulose (TLC Reagent Grade, J. T. Baker, Phillipsburg, NJ) using a vortex mixer (~1 min), and pelletized under 27000 kg in a 3.2 cm diameter press. The resulting ~1 mm thick pellets were mounted in 5 x 5 cm slide frames for analysis. Two pellets were made from each sample to permit estimation of precision.

Automated analyses were accomplished using a silver-filtered, silver secondary source excited by a tungsten anode x-ray tube operated at 40 kV and 14 mA (Model 810, Kevex, Inc., Burlingame, CA). A 16-position vacuum sample changer permitted automatic sequential analyses of multiple samples. The detector was an 80 mm² x 5 mm Si(Li) diode having 200 eV resolution at 6.4 keV (Kevex, Inc.). A computer-based multichannel analyzer (Model 4410, Nuclear Data, Palatine, IL) served to accumulate data and record it on tape for off-line data reduction. The data reduction program (2) used the fluorescent Fe K_α and the scattered Ag K_α peaks for energy scale definition, and analyzed the fluorescent peaks of 24 elements in the 3-17 keV region. Peak analysis using a direct integration method (3) avoided the necessity of estimating background intensities in order to obtain reliable net peak areas. The spectrometer had been previously calibrated for the elements being determined using identical excitation and detection conditions and thin single or dual element standards (Micromatter, Inc., Seattle, WA).

Results

Precisions of the uranium and thorium determinations estimated from the duplicate sample pellets are tabulated in Table I. The slightly greater uncertainty in the uranium analyses resulted from correction of rubidium peak interferences. Accuracies of the uranium determinations as estimated from blind analyses of three ERDA-NBL uranium ore standards (102, 103 and 42-4) and from corresponding uranium determinations by delayed neutron activation indicated a negative relative bias of -15%. Most of this bias was found to result from error in the thin sample uranium sensitivity factor. The error was readily detected from a subsequent multi-element plot of L_α thin film standard sensitivities which showed an anomaly for uranium. An erroneous estimate of mean sample particle sizes could have also accounted for part of the observed bias. Typical relative accuracies for other elements using the same analytical approach have been on the order of 5-6% (1).

TABLE I
PRECISION OF URANIUM PROCESS
SAMPLE ANALYSES USING SAP3

	<u>URANIUM</u>	<u>THORIUM</u>
Number of Sample Pairs	57	28
Concentration Range (ppm)	36-4480	110-2800
Avg Rel Std Dev From Mean	2.5%	1.6%

ANALYTICAL PARAMETERS FOR URANIUM

Current x-ray instrumental capabilities suggest consideration of several analytical parameters before initiating large-scale uranium analyses, including a) choice of M, L, or K-series uranium x-rays; b) choice of x-ray detection with a diffracting crystal, a semiconductor detector, a scintillation counter or a proportional counter; c) choice of radioisotope or x-ray tube excitation; and d) analysis in the laboratory, field, or in-situ.

The choice of M, L, or K-series uranium x-rays greatly affects the geometry and sample preparation requirements due to the different x-ray attenuations and resulting large differences in effective sample volumes. Table II lists approximate values of some parameters for the three x-ray series. Relative sample volumes were computed from the self-absorption half-ranges by assuming the indicated sample diameter and in the case of the K-series, a truncated conical volume defined by the indicated solid angle. Although the use of uranium K x-rays allows a much greater sample mass to be analyzed, the corresponding low photoelectric cross-section offsets any sensitivity advantage. Since detection limits are limited by background intensities, the Compton scatter cross-section is also included and used to estimate a figure of merit (Table II) for the three x-ray series. The advantage indicated for uranium M x-rays is relatively small, especially when considering the additional problems of representative sampling and particle size effects. It should also be noted that the Compton cross-sections are only generally related to spectral background, and thus do not likely reflect accurate relative background intensities at the specific uranium M_{α} , L_{α} , and $K_{\alpha 1}$ peak positions.

Relative particle size effects for the three x-ray series are illustrated in Figure 1 as computed from the equations of Berry et al (4). As indicated, the effects are significant in the 5-100 μ , 200-5000 μ , and >5000 μ size ranges for M, L, and K-series

TABLE II
COMPARISON OF URANIUM X-RAY LINES

	ENERGY (keV)	SELF-ABSORPTION HALF-RANGE (cm)	RELATIVE SAMPLE VOLUME (v) (cm ³)	COMPTON SCATTER CROSS-SECTION (σ) (cm ² /g)	PHOTOELECTRIC (τ) CROSS-SECTION (cm ² /g)	RELATIVE FIGURE OF MERIT (τv/√σv)
M-SERIES	3	0.0012	0.00094	0.082	660	71
L-SERIES	14	0.057	0.045	0.15	84	46
K-SERIES	98	3.4	20.3	0.14	4.1	49

(a) COMPUTED FOR A 1cm DIA SAMPLE SPOT, AND A SOLID ANGLE OF $0.0625/4\pi$

(b) FOR 5.9 keV (^{55}Fe), 22 keV (^{109}Cd), AND 122 keV (^{57}Co) EXCITATIONS, RESPECTIVELY

x-rays respectively. The degree of sample compaction is also shown to be significant and must be considered when powder samples are being analyzed directly.

Figure 1. Particle Size Effects in Uranium Ore Analysis by XRF.

The choice of x-ray detectors depends on the x-ray series being analyzed. Uranium M x-rays usually require wavelength-dispersive analysis for adequate peak resolution as illustrated in Figure 2. A variety of diffracting crystals may be used in this energy region, the most common being LiF(200) and Pentaerythritol (PET). Energy-dispersive analysis with a Si(Li) semiconductor detector would suffer from large potassium and possible argon interferences in direct ore analysis unless a chemical separation were first done and the sample analyzed in vacuo.

Figure 2. Wavelength and Energy Dispersive Detection of Uranium M-Series X-rays.

A similar spectral comparison of uranium L x-rays in Figure 3 indicates comparable resolution can be achieved by either wavelength or energy dispersive analysis at 14 keV. The principal interference to the uranium L_{α} peak comes from Rb, and to the $L_{\beta 1}$ from Mo. Corrections for these interferences can usually be made such that they have little effect unless uranium is near its detection limit. Analysis of uranium L x-rays with scintillation crystals and matched filters and with gas proportional counters has also been common, particularly before the development of higher-resolution Si(Li) detectors in the last decade.

Figure 4 illustrates the spectrum obtained from uranium K x-rays using a weak ^{57}Co excitation source. The large Compton peak at ~ 85 keV can be shifted somewhat with variations in geometry, but invariably contributes significantly to the background of the U $K_{\alpha 1}$ peak. Semiconductor detectors offer the most specific means of analyzing uranium K x-ray spectra, although NaI(Tl) scintillation counting of ^{57}Co -excited uranium solutions reportedly gave significant net signals at concentrations as low as several hundred ppm (5). Thin Ge(Li) or intrinsic Germanium detectors

Figure 3. Wavelength and Energy Dispersive Detection of Uranium L-Series X-rays.

Figure 4. Cobalt-57 Excited X-ray Fluorescence Spectrum of Uranium Ore.

probably offer minimum background and maximum efficiency for detection of the 98 keV x-rays, with over 30 times the efficiency of a Si(Li) detector of comparable size.

COMPARISON OF URANIUM ANALYTICAL CAPABILITIES

A comparison of thin sample XRF analyses for uranium is presented separately from that for bulk ore analysis due to inherent analytical differences. For example, samples from U-fuel processing, ore and tailings leaches, and chemically concentrated environmental samples result in filter-collected deposits which are thin relative to uranium M x-ray penetration. A comparison of such analyses is given in Table III, using various excitation and detection combinations for both M and L series x-rays. The comparisons were made from recent literature data and from data generated by general purpose x-ray instruments without any modifications to enhance uranium detectability.

TABLE III
COMPARISON OF THIN SAMPLE XRF ANALYSES FOR URANIUM

PEAK	EXCITATION	DETECTION	COUNT RATE (c/sec)	SENSITIVITY (C · cm ² / μg · sec)	60 sec 3σ DETECTION LIMIT (μg/cm ²)	REFERENCE
U M _α	Cr TUBE, 2.2 kW	PET		3.8	0.15	MILLER (6)
		LiF (200)		26.0	0.045	MILLER (6)
U M _β	Cr TUBE, 2.2 kW	PET		6.0	0.096	MILLER (6)
		LiF (200)		41.0	0.029	MILLER (6)
U M _{α,β}	Ti SECONDARY (1.5 kW W-TUBE)	Si(Li)	200	54.0	0.039	THIS WORK
U M _{α,β}	⁵⁵ Fe, 35 mCi	Si(Li)	300	2.4	0.33	THIS WORK
U L _α	PI TUBE, 2.2 kW	LiF (200)		23.0	0.26	MILLER (6)
U L _α	Rh TUBE, 35 W.	Si(Li)	6500	16.0	0.43	LAMBERT, et al.
	Rh TUBE, (PULSED)	Si(Li)	7100	18.0	0.41	LAMBERT, et al.
U L _α	Ag SECONDARY (2.2 kW W-TUBE)	Si(Li)	900	10.0	0.052	THIS WORK
U L _α	Mo SECONDARY (2.2 kW, W-TUBE)	Si(Li)	1000	23.0	0.037	THIS WORK
U L _α	¹⁰⁹ Cd, 57 mCi	Si(Li)	1100	11.0	0.041	THIS WORK
U L _α	²⁴¹ Am, 100 mCi	Si(Li)	60	0.13	2.1	THIS WORK

Surprisingly similar low detection limits of 0.03-0.05 μgU/cm² were achieved with the LiF(200) detector crystal at the M_α and M_β lines, and with Si(Li) detectors using the combined M_{α,β} (Ti secondary excitation) and the L_α lines (Mo and Ag secondary and ¹⁰⁹Cd excitation). The anomaly in the M_α and M_β sensitivities resulted from the argon K absorption edge of the proportional counter gas. Although Ti secondary excitation with Si(Li) detection may appear comparable to the wavelength dispersive capabilities, the poorer resolution illustrated in Figure 2 and the resulting interferences discount much of the M_{α,β} analytical merit. Although Miller (6) reported superior capabilities for uranium analysis using M versus L x-rays with wavelength dispersive techniques, comparable L x-ray capability is demonstrated using energy-dispersive detection. The low power DC and pulsed Rh tube excitation contributed a high background which could have been reduced by greater filtration. However, the tube's power restrictions clearly limited its usefulness for thin samples despite the potential high count rate capabilities of the system (7). The Ag secondary source and ¹⁰⁹Cd isotopic source gave nearly identical results, while the Mo-secondary source showed greater merit due to its more optimum exciting energy and hence greater sensitivity. The ²⁴¹Am source was heavily filtered to eliminate excitation peaks below 60 keV, and was thus a poor choice for uranium L_α x-ray excitation as Table III indicates.

A similar comparison is made in Table IV for thicker samples having significant self-absorption. Again, similar low 1-min detection limits of 1.6-3.9 ppm were obtained using various

TABLE IV
COMPARISON OF BULK SAMPLE XRF ANALYSES FOR URANIUM

PEAK	EXCITATION	DETECTION	COUNT RATE kc/sec	SENSITIVITY (C/S - ppm)	60 sec 3 σ DETECTION LIMIT (ppm)	SAMPLE	REFERENCE
U M $_{\alpha}$	Cr TUBE, 2.5 kW	PET		1.1	1.6	71 mg/cm ²	HATHAWAY, et al. (8)
U M $_{\alpha,\beta}$	⁵⁵ Fe, 35 mCi	Si(Li)	500	0.0093	46.0	63 mg/cm ²	THIS WORK
U M $_{\alpha,\beta}$	Ti SECONDARY (1.5 kW W-TUBE)	Si(Li)	1000	0.15	20.0	63 mg/cm ²	THIS WORK
U L $_{\alpha}$	Mo TUBE, 2.5 kW	LiF (220)		~4.4	2.3	510 mg/cm ²	JAMES (9)
	Rh TUBE, 12 W	Si(Li)	14,000	0.19	32.0	63 mg/cm ²	LANBERT, et al.
	Rh TUBE, 35 W (PULSED)		20,000	0.38	25.0	63 mg/cm ²	LANBERT, et al.
	Ag SECONDARY (2.7 kW W-TUBE)		2500	0.53	3.6	63 mg/cm ²	THIS WORK
	Mo SECONDARY (2.7 kW, W-TUBE)		2400	1.14	2.8	63 mg/cm ²	THIS WORK
	¹⁰⁹ Cd, 57 mCi		1400	0.50	3.9	63 mg/cm ²	THIS WORK
	¹⁰⁹ Cd, 50 mCi		3000	0.56	20.0	IN-SITU, UNDER WATER	WOGMAN, et al. (12)
	²⁴¹ Am, 100 mCi		340	0.0057	61.0	63 mg/cm ²	THIS WORK
	¹⁰⁹ Cd, 3mCi	NaI(M), 2r + Y MATCHED FILTERS		0.075	~300.0	FIELD OR IN-SITU	COLUMBIA SCIENTIFIC
	¹⁰⁹ Cd, 3mCi	PROPORTIONAL COUNTER		0.0033	~400.0	FIELD OR IN-SITU	PRINCETON γ -TECH
U K $_{\alpha}$	⁵⁷ Co 0.5 mCi	INTRINSIC Ge	170	0.00071	670.0	1.5 g/cm ²	THIS WORK

combinations of tube and isotope excitation and wavelength and energy dispersive detection. The samples in Table IV were infinitely thick for uranium M x-rays, and the wavelength dispersive detector gave superior sensitivities and detection limits by a factor of ten or more. Direct tube excitation of uranium M x-rays for energy dispersive analysis may somewhat increase the sensitivity and detection limits for U M $_{\alpha,\beta}$, but would probably not approach the wavelength dispersive XRF capabilities for sensitivity, detection limits, or minimal interferences.

The best analyses using uranium L x-rays indicate some trade-offs between the high exciting power of direct Mo tube excitation and the low background achieved with a Mo secondary source. Although inherently less sensitive, the secondary source spectrum can be analyzed by a Si(Li) detector to give comparable detection limits due to the larger solid angle possible with energy dispersive detectors. Use of a Si(Li) detector with direct Rh tube excitation also has good sensitivity, especially in the pulsed tube mode, but suffers from high background under the L $_{\alpha}$ peak. Optimum filtering of the exciting spectrum and use of a high power tube would greatly improve these detection limits, especially with the high count rate capability available in the pulsed mode. Excitation by Ag-secondary and ¹⁰⁹Cd sources gives nearly identical results, surpassed only by the Mo-secondary fluorescer for optimum energy-

dispersive analysis. A ^{109}Cd source used in an in-situ seabed analyzer gave comparable sensitivities to the laboratory system, but poorer detection limits in the combined water-sediment sample matrix. These results were obtained under ~10m water (12). Excitation by ^{241}Am again yielded low sensitivity for uranium L_{α} x-rays.

The two commercially available field or in-situ analyzers using matched filter scintillation counting and sealed gas proportional counting differ greatly in sensitivity, but are still similar in detection limit, due to background or "blank" differences. Their advantages in terms of cost, portability and ruggedness may offset their analytical weaknesses (detection limits; potential interferences) for many applications. Two reviews (10,11) of portable XRF technology summarize these non-Si(Li), non-dispersive analysis methods. Current applications of Si(Li), Ge(Li), or intrinsic germanium detectors to rugged field uses (12-14) suggest that current laboratory capabilities may soon be available for field and in-situ XRF analysis.

K-series XRF for uranium analysis is inherently limited by high Compton/photoelectric cross section ratios, and further limited by available excitation sources. Cobalt-57 is probably the best excitation source (85% 122 keV; 11% 136 keV), and could be increased in activity by at least a factor of 20 over that indicated in Table IV. Count rates limit the ultimate excitation activity. Even if uranium K-series XRF is limited to concentrations above 100 ppm, its potential avoidance of elemental interferences, particle size effects, and sampling errors (relative to less penetrating radiation) may make it attractive for many field or in-situ applications.

A number of non-fluorescent activity counting methods for uranium determination are presented in Table V for comparison with the capabilities of XRF methods. Direct analysis of uranium daughters in equilibrium with ^{238}U allows 250 ppm uranium to be detected in 1-min intervals with a Ge(Li) spectrometer. Detection of ^{214}Bi γ -rays permits much more sensitive detection of uranium, but is subject to serious errors from disequilibrium. Neutron activation with a ^{252}Cf source permits detection of ~100 ppm U in 10-min counts using low energy γ -ray analysis, and even lower concentrations in much shorter times if delayed neutrons from uranium fission are measured. The remaining methods using reactor neutrons achieve much lower detection limits, but are clearly limited to laboratory applications and require greater analytical times per sample.

TABLE V
URANIUM DETERMINATION BY NON-FLUORESCENT COUNTING

METHOD	PEAK (Kev)	DETECTION	SENSITIVITY (C/S · % U)	3 σ DETECTION LIMIT (ppm U)	REFERENCE
DIRECT COUNTING	93 (²³⁴ Th)	Ge (Li)	0.18	~1000 (60 min)	MUBARAKMAND (15)
DIRECT COUNTING	63 (²³⁴ Th)	INTRINSIC Ge	---	1000 (4 min)	USGS (16)
DIRECT COUNTING	1001 (^{234m} Pa)	Ge (Li)	7.8	250 (1 min)	BRODZINSKI et al. (17)
DIRECT COUNTING	1120, 1760 (²¹⁴ Bi)	2-NaI (TI)	950	0.13 (1 min) 0.004 (10 ³ min)	WOGMAN et al. (18)
²⁵² Cf NAA	219 (¹³⁹ Xe)	Ge (Li)	60	> 2900 (41 sec)	BRODZINSKI et al. (17)
²⁵² Cf NAA	75 (²³⁹ U)	INTRINSIC Ge	~30	100 (10 min)	USGS (16)
²⁵² Cf DNAA	DELAYED NEUTRONS	³ He n-DETECTORS	480	< 100 (11 sec)	IRT CORP (19)
REACTOR NAA	75 (²³⁹ U)	Ge (Li)	---	< 1 (5 min)	HANCOCK (20)
REACTOR EPITHERMAL NAA	228, 278 (²³⁹ Np)	Ge (Li)	---	~ 0.1 (8 min)	STEINNES (21)
REACTOR RADIOCHEMICAL NAA	816, 1597 ¹⁴⁰ La	Ge (Li)	---	0.001 (1 hr)	LAUL et al. (22)

SUMMARY

Nearly all of the XRF methods listed in Table IV provide suitable sensitivities and detection limits for rapid assay of uranium in commercial grade ores ($\geq 0.01\%$ U). Parts-per-million uranium detection limits can be routinely achieved using secondary source or isotope excitation with Si(Li) detectors, or direct tube excitation with wavelength dispersive detectors, and perhaps by certain other optimized combinations of the excitation and detection methods considered here. Careful attention should be paid to sample parameters such as self-absorption, particle size, and sample compaction, if accurate results are to be obtained. Rapid quantitative uranium ore analyses may be easily obtained from direct comparison of fluorescent peak intensities with those from matching ore standards. When such standards are not readily available, rapid and precise quantitative analyses may also be done using mathematical methods to compute the concentrations in the unknown geological matrix. XRF capabilities for uranium ore analysis appear to exceed those of direct gamma-ray spectrometry or of methods using ²⁵²Cf neutron-induced fission/activation of the uranium. Reactor

neutron activation and delayed neutron activation analysis methods are superior to XRF in the laboratory.

ACKNOWLEDGMENTS

The authors appreciate the cooperation of M. C. Lambert and M. W. Urie in comparative sample analyses, and information and suggestions from J. W. Binns, J. R. Rhodes and A. G. Miller.

REFERENCES

1. K. K. Nielson, Matrix Corrections for Energy Dispersive X-ray Fluorescence Analysis of Environmental Samples with Coherent/Incoherent Scattered X-rays," *Anal. Chem.* 49, 641 (1977).
2. K. K. Nielson, "SAP3: A Computer Program for X-ray Fluorescence Data Reduction for Environmental Samples," BNWL-2193, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, April, 1977.
3. K. K. Nielson, "Application of Direct Peak Analysis to Energy Dispersive X-ray Fluorescence Spectra," BNWL-2277, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, July, 1977.
4. P. F. Berry, T. Furuta and J. R. Rhodes, "Particle Size Effects in Radioisotope X-ray Spectrometry," *Advances in X-Ray Anal.* 12, 612 (1969).
5. S. Forberg and A. R. De Ruvo, "Analysis of Uranium Solutions by Scintillation Detection of X-ray Fluorescence Excited by Co-57 122 keV γ -Rays," in *Proc. Symposium Radiochem. Methods of Analysis*, Salzburg, 1964, Vol II, IAEA, Vienna, 1965, p. 485.
6. A. G. Miller, "Analytical Utility of the M Series X-ray Emission Lines Applied to Uranium, Neptunium, Plutonium, and Americium," *Anal. Chem.* 48, 1976 (1976).
7. J. E. Stewart, H. R. Zulliger and W. E. Drummond, "Energy Dispersive X-ray Fluorescence Spectrometry at High Count Rates: Pulsed Tube Excitation and Recovery of Resolution by Computer Processing," *Advances in X-Ray Anal.* 19, 153 (1976).
8. L. R. Hathaway and G. W. James, "Use of Chelating Ion-Exchange Resin in the Determination of Uranium in Ground Water by X-ray Fluorescence," *Anal. Chem.* 47, 2035 (1975).

9. G. W. James, "Parts-per-Million Determinations of Uranium and Thorium in Geologic Samples by X-ray Spectrometry," *Anal. Chem.* 49, 967 (1977).
10. J. R. Rhodes, "Radioisotope X-ray Spectrometry," *Analyst* 91, 683 (1966).
11. J. R. Rhodes, "Portable Radioisotope X-ray Analyzers--Techniques and Applications," *Isotop. Rad. Technol.* 8, 153 (1970-71).
12. N. A. Wogman and K. K. Nielson, "In-Situ Parts-per-Million Analysis of Marine Sediments by X-ray Fluorescence Techniques," *Proceedings, MTS-IEEE Symposium, Oceans '76*, Washington, D.C., Sept., 1976, paper 12A.
13. H. L. Nielson, N. A. Wogman and R. L. Brodzinski, "In-Situ Subterranean Gamma-Ray Spectroscopy," *Nucl. Inst. Meth.* 143, 385 (1977).
14. D. A. Gedcke, R. Rolle and P.J.D. Lloyd, "A Portable Gold Analyzer for In-Situ Ore Analysis," *Advances in X-Ray Anal.* 21, (1978).
15. S. Mubarakmand, P. Chaudhry and F. I. Nagi, "Absolute Determination of Uranium Concentrations in Rocks by Gamma-Ray Spectroscopy," *Nucl. Inst. Meth.* 140, 133 (1977).
16. U. S. Geological Survey, "Intrinsic Germanium, ^{252}Cf Borehole Sonde Used for Uranium Exploration," *Californium-252 Progress*, No. 21, Dec., 1976, p. 15, USERDA.
17. R. L. Brodzinski and N. A. Wogman, "Californium-252 In-Situ Activation and Photon Detection Techniques for Uranium Ore Deposit Evaluation," *IAEA/SM/208-50* (1976).
18. N. A. Wogman, D. E. Robertson and R. W. Perkins, "A Large Detector, Anticoincidence Shielded Multidimensional Gamma-Ray Spectrometer," *Nucl. Inst. Meth.* 50, 1 (1967).
19. IRT Corporation, " ^{252}Cf -Based Borehold Logging System for In-Situ Assaying of Uranium Ore," *Californium-252 Progress*, No. 21, Dec., 1976, P. 15, USERDA.
20. R.G.V. Hancock, "Low Flux Multielement Instrumental Neutron Activation Analysis in Archaeometry," *Anal. Chem.* 48, 1443 (1976).

21. E. Steinnes, "Simultaneous Determination of Uranium, Thorium, Molybdenum, Tungsten, Arsenic, and Antimony in Granitic Rocks By Epithermal Neutron Activation Analysis," Anal. Chem. 48, 1440 (1976).
22. J. C. Laul, "Neutron Activation Analysis in Geological Materials," BNWL-SA-6280, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, May, 1977.