Determination of U, S, V, Cu, Zn, Sr, Mo, and Ce in Carbonate Rocks by Wavelength Dispersive X-Ray Fluorescence Spectrometry and Inductively Coupled Plasma Optical Emission Spectrometry

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ABSTRACT

The paper describes a simple, rapid, accurate, and cost-effective wavelength dispersive x-ray fluorescence spectrometry (WDXRFS) methodology as an alternate to complimentary techniques such as fluorimetry and inductively coupled plasma optical emission spectrometry (ICP-OES) for the determination of U, S, V, Cu, Zn, Sr, Mo, and Ce in carbonate rocks. The WDXRF spectrometer is calibrated using three matrix matching international certified reference materials (CRMs) of LKSD-1, LKSD-2, and LKSD-3 Carbonate Lake Sediment, along with a few in-house standards. The S K_{α} , V K_{α} , Zn K_{α} , Cu K_{α} , Sr K_{α} , Mo K_{α} , Ce L_{α} , and U- L_{α} lines were considered for quantifying the elements. The LKSD-1 CRM was also used as the test sample to validate the analytical methodology.

By using WDXRFS, accuracies of better than 4% were achieved, except for U (7.2% at 10 ppm) and Mo (10%, at 10ppm). For ICP-OES it was better than 5%, except for Mo (10.0%, at 10 ppm) and Ce (11.1%, at 10 ppm). The precision for WDXRFS was better than 3%, except for Mo (3.7%, at 10 ppm) and U (5.2%, at 10 ppm); for ICP-OES it was better than 5%, except for Mo (14.2%, at 10 ppm), Ce (6.2%, at 10 ppm), and U (8.5%, at 10 ppm). The limits of detection (LODs) were also calculated for both techniques. The accuracy, precision, and LODs obtained show the viability of this simple, non-destructive, and rapid WDXRFS methodology as an alternate to complimentary wet chemical techniques for the determination of the above-mentioned elements in carbonate rocks.

A large number of carbonate rock samples from Tumalapalle have been analyzed for uranium and other trace elements. Wavelength dispersive X-ray fluorescence spectrometry (WDXRFS) is thought to be the right choice of methodology for the rapid analysis of large numbers of samples. However, matrix matching reference standards need to be prepared in-house for calibration of WDXRFS since CRMs rich in carbonate-containing trace elements, including uranium, are not available. The complimentary techniques of ICP-OES and fluorimetry have been used for the preparation of in-house standards of carbonate rocks from the Tumalapalle area along with three international CRMs for the calibration and quantitative estimation of trace elements, including uranium and sulfur.

WDXRFS is a suitable non-destructive method for the rapid determination of a wide range of concentrations (ppm to %) of different elements in geological materials such as rocks, minerals, and ores, and is regarded as one of the most important analytical tool for the geochemical determination of major, minor, and selected trace elements (4,5). WDXRFS analysis produces results with high precision using a simple and rapid sample preparation method involving finely ground (-200 mesh or < 63 micron) powdered pellets. However, the use of WDXRFS requires many matrix matching standard samples for reference and calibration. The determination of different components, such as sulfur in silicate and carbonate rocks by XRF

INTRODUCTION

The rapid, cost-effective, precise, and accurate determination of uranium and some other trace elements in different kinds of geological materials is very significant at almost every stage of exploration from orientation, reconnaissance, and semi-detailed surveys to exploitation of the desired mineral. These data are required for evaluation of the geological terrain to narrow down the target, geo-modeling, assessment of grade, tonnage, etc. Uranium is associated along with

sulfide-bearing minerals like pyrite (FeS_2), chalcopyrite (CuFeS_2), and molybdenite (MoS_2), etc., within the host carbonate rocks (dolostones) found near Tumalapalle, Cuddapah district, Andhra Pradesh, India (1). Hence, analysis of elemental sulfur in sulfide-bearing carbonate rocks plays a major role in identifying the type and nature of mineralization. The Atomic Minerals Directorate for Exploration and Research (AMD) has identified unique types of uranium deposits hosted in carbonate rock (dolostone) near Tumalapalle (2) and in brecciated limestone near Gogi, Gulbarga district, Karnataka, India (3).

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using the fusion bead sample preparation method, was reported by Milada (6).

In the present study, a powder pelletization sample preparation technique was used for the determination of sulfur along with U, V, Cu, Zn, Sr, Mo, and Ce in carbonate rocks. The powder pelletization sample preparation technique has several advantages over the fusion bead method since it is simple, fast, inexpensive, and non-destructive, the chances of sample dilution is minimal and provides quick feedback to the exploration program (7-9).

Various methods such as gamma ray spectrometry, fluorimetry, atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and WDXRFS are used for the determination of uranium in geological samples. Fluorimetric determination of trace level uranium is a popular technique due to its high sensitivity and specificity and is widely used for the analysis of a variety of geological material (10-11). The majority of reported works deal with the determination

of uranium in different rocks after selective separation of uranium because many elements quench fluorescence (12). Therefore, separation and pre-concentration of uranium is required for its determination by fluorimetry in a complex matrix. Further AAS, ICP-OES, and ICP-MS are mostly used for the determination of trace elements such as V, Cu, Zn, Sr, Mo, Ce, and S and require sample dissolution in aqueous/acid media (13).

The present study aims at developing an alternate rapid, simple, accurate, and precise methodology for the characterization of different types of carbonate rocks by WDXRFS, while validating the obtained data by fluorimetry for uranium and by ICP-OES for other trace elements. The accuracy, precision, and limits of detection achieved for U, V, Cu, Zn, Sr, Mo, Ce, and S are well documented and are comparable with ICP-OES. These samples were then used as internal reference standards for calibration of the WDXRFS prior to their analysis.

EXPERIMENTAL

Instrumentation

WDXRFS

A sequential wavelength dispersive x-ray fluorescence spectrometer Model MagiX-PRO: PW2440 (PANalytical, Netherlands), equipped with an end window Rh anode, having a rated capacity of 4 kW (60 kV/125 mA) instrument and a 4 kW rhodium end window x-ray tube, was used in this study. The instrumental parameters such as spectral lines, analyzing crystals, collimators, detectors, peak and background positions, voltage (kV), current (mA), and counting times are listed in Table I.

ICP-OES

A Model ULTIMA-2 inductively coupled plasma optical emission spectrometer (Horiba Jobin Yvon, France), was used for this study. The instrumental specifications/parameters and operating conditions are listed in Table II.

Pellet Fluorimeter

An ECIL filter fluorimeter (Electronic Corporation of India Limited, India), having an excitation light source (Hg vapor lamp) wavelength of 365 nm and equipped with a PMT detector arranged at zero

TABLE I
Instrumental Parameters for WDXRFS Using 4 kW End Window Rh Tube

Element		2 θ Position		Counting time (sec.)			Analyzing Crystal	Detector ^a	Collimator	kV	mA
X-ray Line	Peak	Bg 1	Bg 2	Peak	Bg 1	Bg 2					
SK $_{\alpha}$	110.7208	-0.7126	1.2358	120	10	10	Ge 111	GFPC	300 μ m	30	100
VK $_{\alpha}$	69.3200	-0.0402	-	120	20	-	LiF 220	GFPC	300 μ m	60	50
CuK $_{\alpha}$	65.5316	0.148	-	60	10	-	LiF 220	Duplex	150 μ m	60	50
ZnK $_{\alpha}$	60.5262	-0.459	-	30	10	-	LiF 220	SC	150 μ m	60	50
SrK $_{\alpha}$	25.1086	0.4338	-	30	10	-	LiF 220	SC	150 μ m	60	50
MoK $_{\alpha}$	28.8490	0.3918	-	120	10	-	LiF 220	SC	150 μ m	60	50
CeL $_{\alpha}$	79.1714	-0.5574	-	60	10	-	LiF 200	Duplex	300 μ m	60	50
U-L $_{\alpha}$	37.2578	-0.3348	0.4508	120	10	10	LiF 220	SC	300 μ m	60	50

^a GFPC = Gas flow proportional counter.

SC=Scintillation counter.

Duplex=Gas flow proportional counter and sealed xenon detector.

angle geometry, was used for the uranium fluorescence intensity measurements. A characteristic uranium fluorescence of 555 nm emanating from the sample pellet was measured.

Sample Preparation

WDXRFS

An amount of 200-300 g (3-4 inches) of sample was crushed to 4 - 6 mesh size by a jaw crusher, then a 10-g sample was taken and further ground to -200 mesh using a laboratory-type disc mill and the powders were homogenized. Smaller representative volumes of the homogenized powders were obtained by coning and quartering. The powdered samples (1 g) were spread uniformly over a 20-g boric acid bed in a cylindrical sample die, and finally pelletized in a semi-automatic pelletizer at a pressure of 20,000 kg/cm² resulting in a solid pellet of 41 mm in diameter. Thus, flat and homogeneous pellets of both the sample and the CRMs were obtained (4).

ICP-OES

The powdered sample (0.5 g) was transferred into a platinum dish and incinerated in a furnace at 650 °C for one hour to remove any organic matter. Then, it was treated with 5 mL of 40% HF and 2 mL of concentrated HNO₃ and evaporated to dryness in a boiling water bath. The process was repeated three times with 3 mL of HF and 2 mL of HNO₃. The sample was then treated three times with HNO₃. The residue was dissolved in HNO₃ solution and made up to 100 mL volume maintaining a final acidity of 2% (10,12). However, the solutions for the determination of sulfur were prepared by fusion of the samples with sodium peroxide.

Pellet Fluorimetry

The powdered rock sample (1.0 g) was treated with 3 mL HF and 5 mL HNO₃ three times and digested with 10% HNO₃ in a platinum crucible. Uranium was extracted with ethyl acetate using aluminium nitrate as the salting out agent. The aliquot from the organic layer to be analyzed was dried under an infrared lamp, combined with a flux (Na₂CO₃: NaF = 4:1) in

a platinum planchet, and heated to approximately 850 °C. After cooling, the fused pellet was used for intensity measurements in the filter fluorimeter.

METHODOLOGY

WDXRFS

Calibration Standards

The instrument was calibrated using the three international CRMs LKSD-1, 2, and 3 Carbonate Lake Sediment (Canada Centre for Energy and Mineral Technology, (CANMET), Canada) (13) and in-house reference standards prepared from carbonate rock samples (from the proposed uranium mining project, Tumallapalle, Cuddapah district, A.P., India). These samples were analyzed several times for V, Cu, Zn, Sr, Mo, Ce, and S by ICP-OES and AAS and for uranium by fluorimetry. The in-house standards, having similar matrices, helped to analyze the unknown samples with lower concentrations of these metals. Calibration was made using corrected net peak intensity (K counts/s) against concentration. The calibration graphs for determining U, S, V, Cu, Zn, Sr, Mo, and Ce in carbonate rocks by WDXRFS are given in Figure 1 (A-H).

Correction for Spectral Overlap

Pure elements were used to determine the degree of spectral line overlap and for calculation of the corrections. The net intensity (R_{ji}) of the interfering element (j) was measured at the 2 theta angle for the element (i) to be determined. Then the net intensity of a non-interference line (R_j) of the interfering element (j) was measured. The ratio of R_{ji}/R_j was taken as line overlap correction factor. Suitable software "Super Q, 4.0D version" (PANalytical B.V., Almelo, The Netherlands) was used to take care of dead time correction and inter-element matrix effects.

TABLE II

Instrumental Specifications and Operating Conditions of ICP-OES

Parameters	
Model	Horiba Jobin Yvon ULTIMA-2
Mounting	Czerny - Turner
Focal Length	One meter
Grating grooves	4320 g/mm, 2400 gr/mm
Order of measurement	1 st order
1st Order resolution	0.005 nm
Type of RF Generator	Solid state generator
Observation	Radial viewing
Frequency of Generator	40.68 MHz
Generator power	1200 W
Plasma flow rate	12 L/min
Sheath gas flow rate	0.2 L/min
Nebulizer gas flow rate	0.68 L/min
Sample uptake	Meinhard Nebulizer
Type of spray chamber	Cyclonic

Fig. 1. Calibration curves of S, V, Cu, Zn, Sr, Mo, Ce, and U drawn by using different international and in-house standards for DXRFS.

The UL_{α} , SK_{α} , VK_{α} , CuK_{α} , ZnK_{α} , SrK_{α} , MoK_{α} , and CeL_{α} lines, considered to quantify these elements in carbonate rocks as the concentration of the adjacent interfering elements, are much less in the present matrix (Table I). The energy of UK_{α} and CeK_{α} was 97.131 and 34.566 KeV, respectively. When the excitation is done by continuum source alone, the voltage should be such that the tube voltage is at least 3–4 times the excitation potential of the analyte element. In the present study, the instrument used was 60 kV (maximum) which does not permit excitation of UK_{α} and CeK_{α} and, instead, L lines were selected to determine both elements.

ICP-OES/Pellet Fluorimeter

All dilutions were performed using Milli-Q™ water (Millipore Corporation, USA). SupraPur® 40% HF (E. Merck, Germany) and sub-boiled HCl and HNO_3 , GR grade (Merck, Germany), were used. The trace element stock solutions were prepared from high purity oxides (99.99% or 99.999%, Alfa Aesar, U.K) by dissolution in HCl. Uranium stock solution was prepared from uranium nitrate salt (AnalR® grade). First, single-element (1000 $\mu\text{g/mL}$) stock solutions were prepared, and a mixed multi-element standard solution (10 $\mu\text{g/mL}$) was prepared from the

above stock solution by appropriate dilution. Solutions of the CRMs LKSD 1, 2, and 3 were prepared and analyzed.

In ICP-OES, the sample is nebulized and transferred to the argon plasma, decomposed, atomized, and ionized whereby the atoms and ions are excited. Each element emits light at characteristic wavelengths, and these lines can be used for quantitative analysis after a calibration. The light emitted by the plasma contains numerous argon lines and a continuum that extends over the complete wavelength range. These emissions originate from recombination of the Ar ions, electrons, and Bremsstrahlung of the electrons. The matrix can vary the background intensity and its level is measured and corrected. The background correction is applied on both sides of the peak. The background correction points, wavelengths, detection limits (DLs), and background equivalent concentration (BEC) for each element are provided in Table III.

It was observed that during acid digestion of the carbonate rock samples, large quantities of high-purity acids are consumed and quick effervescence may cause some loss due to sputtering. Since these samples contain high amounts of calcium, formation of refractory CaF_2 poses difficulty in

dissolution with 3% HNO_3 . A high calcium content in the sample is known to cause signal suppression during ICP-OES analysis as it cools down the plasma. To overcome these problems, the samples were digested in closed containers in order to avoid sputtering during acid digestion of the high carbonate rock samples. In order to avoid possible formation of CaF_2 , the samples were pretreated with 5% (v/v) HNO_3 , filtered, and further processed with HF and HNO_3 . In order to do away with the signal depression due to the high Ca content, a higher RF power of 1200 W was applied during sample analysis. The determination of total sulfur by chemical means is cumbersome. Since the samples were digested with highly corrosive *aqua regia*, later dissolved in nitric acid, and finally determined by ICP-OES, the optics have to be purged with nitrogen for 3 hours prior to analysis. Sulfur can also be determined by conventional barium sulfate precipitation after fusion with sodium peroxide and water leaching of the fused melt. Excess barium is determined by titration with EDTA (15) or can also be determined by AAS.

RESULTS AND DISCUSSION

The carbonate rock samples, along with CRM LKSD-1, were chemically characterized by AAS, ICP-OES, and fluorimetry. The

TABLE III
Wavelength, Background Correction, and Analytical Conditions for ICP-OES

Ele- ment	Wavelength (nm)	BEC (μg/L)	DL (μg/L)	BGC	Standard (μg/L)		Gain	High Voltage	MP	CP	IT	Exit slit (μm)	Analysis Mode
S	181.978	0.57	0.17	±0.016	10	1.0	100	990	9	5	0.5	15	Gauss
Ce	418.660	0.128	0.95	±0.015	10	1.0	100	710	9	5	0.5	15	Gauss
Cu	324.754	0.10	3.0	+ 0.016	1.0	0.1	100	700	9	5	0.5	15	Gauss
Mo	202.030	0.05	1.5	- 0.009	1.0	0.1	10	800	9	5	0.5	15	Gauss
Sr	407.771	0.05	1.5	- 0.012	1.0	0.1	10	630	9	5	0.5	15	Gauss
V	292.402	0.09	2.7	- 0.016	1.0	0.1	100	590	9	5	0.5	15	Gauss
Zn	213.856	0.02	0.6	- 0.013	1.0	0.1	100	590	9	5	0.5	15	Gauss

BEC: Background equivalent concentration, BGC: Background Correction, DL: Detection limit; BEC x RSD (1%) x 3, MP: Measurement point, CP: Calculated Points, IT: Integration Time (s)

values were obtained with sufficient statistical analysis of the analytical data generated. The certified values of U, S, V, Cu, Zn, Sr, Mo, and Ce in the international standard LKSD-1 and the statistically arrived values in one in-house reference material (FC-155/S-2354) are listed in Table IV. The values obtained by ICP-OES and WDXRFS were in close agreement.

The accuracies achieved (Table V) by WDXRFS were as follows: U: $\pm 7.22\%$, S: $\pm 0.64\%$, V: $\pm 1.15\%$, Cu: $\pm 2.27\%$, Zn: $\pm 0.30\%$, Sr: $\pm 2.40\%$, Mo: $\pm 10.0\%$, and Ce: $\pm 3.70\%$. The accuracies achieved by ICP-OES

were: S: $\pm 1.91\%$, V: $\pm 4.60\%$, Cu: $\pm 4.55\%$, Zn: $\pm 3.93\%$, Sr: $\pm 2.80\%$, Mo: $\pm 10.0\%$, and Ce: $\pm 11.11\%$, which is comparable with their recommended values. The accuracy and precision achieved by the fluorimetry technique for U were $\pm 1.03\%$ and 8.54% , respectively.

The precision of the instrument was evaluated by six replicate analyses of the international standard reference material LKSD-1. The average concentrations and the %RSDs (coefficient of variation) are listed in Table V. It can be seen that the %RSDs for the elements determined by WDXRFS were as

follows: U: 5.21%, S: 0.7%, V: 1.04%, Cu: 1.19%, Zn: 0.27%, Sr: 0.33%, Mo: 3.66%, and Ce: 2.15%. The precisions by ICP-OES were S: 0.95%, V: 1.38%, Cu: 3.76%, Zn: 0.8%, Sr: 0.79%, Mo: 14.17%, and Ce: 6.16%.

The limit of detection (LOD) by WDXRFS was calculated as 8 ppm for U, 100 ppm for S, 5 ppm for V, 2 ppm for Cu, 5 ppm for Zn and Sr, 10 ppm for Mo and Ce by applying $3/m \cdot \sqrt{I_b/t_b}$ ($m = \text{cps}/\%$; I_b = background counts; and t_b = time taken in background) at the 95% confidence limit. The limits of detection (LOD) by ICP-OES were calculated as follows: S: 0.017 $\mu\text{g/L}$, Cu: 3 $\mu\text{g/L}$, Mo: 1.5 $\mu\text{g/L}$, Sr: 1.5 $\mu\text{g/L}$, V: 2.7 $\mu\text{g/L}$, Zn: 0.6 $\mu\text{g/L}$, and Ce: 0.095 $\mu\text{g/L}$. The limit of detection (LOD) was calculated as 0.5 $\mu\text{g/L}$ for U.

The proposed method was employed in the routine analysis of a large number of carbonate rocks collected from the Tumallapalle area, Andhra Pradesh, India. The results obtained are in close agreement with those of ICP-OES and fluorimetry. Samples ($n=11$) with wide concentration ranges of the different elements were analyzed and the results are listed in Table VI and shown in Figures 2, 3, and 4.

TABLE IV
Comparison of Analytical Values of
Certified International Standard LKSD-1 and In-house Standard
FC-155 (S-2354) by WDXRFS, ICP-OES, and Fluorimetry Techniques

Element	Certif. Value ^a	LKSD-1 WDXRFS	ICP-OES	Element	Assigned Value	FC-155 (S-2354) WDXRFS	ICP-OES
S (%)	1.57	1.56	1.54	S (%)	0.85	0.83	0.83
V (ppm)	87	86	83	V (ppm)	170	168	165
Cu (ppm)	44	43	42	Cu (ppm)	135	132	132
Zn (ppm)	331	330	318	Zn (ppm)	5	6	5
Sr (ppm)	250	256	243	Sr (ppm)	556	566	548
Mo (ppm)	10	11	9	Mo (ppm)	210	210	205
Ce (ppm)	27	26	24	Ce (ppm)	10	11	10
U ^b (ppm)	9.7	9	9.8	U ^b (ppm)	48	49	46

^a Certified Value, Govindaraju, 1996.

^b Fluorimetry.

TABLE V
Accuracy and Precision Achieved for International Standard Sample (LKSD-1) by WDXRFS and ICP-OES

Element	Certified Value	WDXRFS				ICP-OES			
		Mean (n=6)	Std. Dev.	CV (%)	Accuracy (%)	Mean (n=6)	Std. Dev.	CV (%)	Accuracy (%)
S (%)	1.57	1.56	0.0103	0.661	0.64	1.54	0.015	0.95	1.91
V (ppm)	87	86	0.8944	1.040	1.15	83	1.14	1.38	4.60
Cu (ppm)	44	43	0.5164	1.192	2.27	42	1.58	3.76	4.55
Zn (ppm)	331	330	0.8944	0.271	0.30	318	2.54	0.8	3.93
Sr (ppm)	250	256	0.8165	0.325	2.40	243	1.92	0.79	2.80
Mo (ppm)	10	11	0.4082	3.656	10.00	9	1.3	14.17	10.00
Ce (ppm)	27	26	0.5477	2.148	3.70	24	1.51	6.16	11.11
U ^a (ppm)	9.7	9	0.5477	5.216	7.22	9.8	0.84	8.54	1.03

^a = U by Fluorimetry   n = Number of determinations, Std. Dev. = standard deviation, %CV = Coefficient of variation.

Accuracy is the percentage of deviation of the arithmetic mean of a set of six values from the certified value.

TABLE VI
Analytical Results for Geological Samples Analyzed by WDXRFS, ICP-OES, and Fluorimetry Techniques.

Elements	AMD-1		AMD-2		AMD-3		AMD-4		AMD-5		AMD-6		AMD-7		AMD-8		AMD-9		AMD-10		AMD-11	
	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP	XRF	ICP
V	12	10	60	54	79	88	210	200	341	330	229	220	245	238	119	124	50	48	38	32	45	50
Cu	825	832	1536	1548	775	780	222	214	125	132	78	88	185	178	34	36	13	14	11	10	5476	5455
Zn	20	22	16	14	7	6	9	8	9	8	7	8	6	8	10	8	65	60	50	54	155	150
Sr	247	252	355	350	331	336	385	378	364	372	461	454	435	442	440	432	262	256	216	220	306	301
Mo	20	18	60	56	105	100	189	194	341	330	225	230	241	236	124	120	46	48	35	38	42	44
Ce	34	36	22	24	16	14	32	30	20	18	26	28	27	26	28	30	14	16	14	16	26	24
S(%)	5.08	4.99	0.44	0.53	0.69	0.77	0.82	0.74	0.6	0.53	0.5	0.47	0.41	0.46	0.5	0.56	0.31	0.38	0.35	0.42	0.25	0.33
	XRF	Fluori	XRF	Fluori	XRF	Fluori	XRF	Fluori	XRF	Fluori	XRF	Fluori	XRF	Fluori	XRF	Fluori	XRF	Fluori	XRF	Fluori	XRF	Fluori
U	14	12	149	142	594	586	225	234	415	408	645	638	340	336	445	440	39	42	14	16	761	750

XRF: WDXRF; ICP: ICP-OES; Fluori: Fluorimetry.

Except for Sulfur, all other elements concentration mentioned here in ppm.

Fig. 2 Comparison of values obtained by Fluorimetry and WDXRFS.

Fig. 3 Comparison of values obtained by ICP-OES and WDXRFS.

The analysis of rock samples by ICP-OES, AAS, and fluorimetry involves laborious sample dissolution, separation, and various analysis steps. However, the sample preparation step for WDXRF is minimal and the technique is very fast in comparison to the other complementary techniques mentioned. About 30 samples can be analyzed by WDXRFS within eight hours and thus provide quick feedback to the uranium exploration project.

The XRF methods of analysis do not require chemical preparation of the samples in a clean room which involves HF digestions. XRF spectrometers are simple to operate for routine analyses and can work unattended overnight and for long periods of time. The XRF method is non-destructive and, apart from the simple sample preparation, the standards so prepared can be preserved and reused even over a period of many years.

In the present study, the powder pelletization sample preparation technique has been adopted in place of the fusion bead technique by using lithium tetraborate/metaborate at 1100°C, and the loss of elemental sulfur by volatilization during fusion at elevated temperatures has been overcome.