The USGS Reference Sample Devonian Ohio Shale SDO–1

U.S. GEOLOGICAL SURVEY BULLETIN 2046

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The USGS Reference Sample Devonian Ohio Shale SDO–1

Edited by JEAN S. KANE

This publication presents a collection of detailed analytical procedures used by some of the laboratories whose data was used to derive recommended concentrations for SDO–1 as a geochemical reference sample, and outlines the statistical evaluation used in the derivation of those concentrations from the total data base.

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[Letters designate the chapters]

The USGS Reference Sample Devonian Ohio Shale SDO–1

Edited by Jean S. Kane

INTRODUCTION

The United States Geological Survey (USGS) has maintained a geochemical reference sample (GRS) program since 1951, when the Fairbairn report on the cooperative analysis of G–1 and W–1 was issued. Many of the reference samples developed and issued to the worldwide geochemical community since then have been igneous rocks whose elemental concentrations are quite well established, making the GRS's comparable to National Institute of Standards and Technology (NIST) certified or standard reference samples (SRM's). For the most part, these igneous rock reference samples have trace element concentrations at rather low levels, approaching average crustal abundances. These materials are quite useful in baseline geochemical applications, but of less value in exploration programs or in studies of ore genesis where higher trace elemental abundances are characteristic of the samples actually being analyzed. These materials are sometimes poorly suited, by virtue of matrix mismatches, for use in studies of metamorphic and sedimentary rocks, including gas and oil shales and coal. USGS has begun developing a number of new reference samples to meet these added needs. This bulletin is devoted to the development of one of these new materials, Devonian Ohio Shale SDO–1. (Note that there is a homonym of this material, the marine sediment SDO–1 issued by the USSR Academy of Sciences (Arnautov, 1987).)

SDO–1, a gas shale, was first introduced in the seventies as a control sample during the Eastern Gas Shale Project sponsored by the U.S. Department of Energy (DOE) (1978), in which the USGS was a participant. The sample is a brownish-black, relatively radioactive shale (40–100 counts/second, or 2–4 times background over 0–200 ft) that weathers blocky and massive in the lower two-thirds of the unit and is less resistant in the upper one-third of the unit. Thin-sections show the shale to be organic-rich with a fine-ground clay matrix and abundant microfossils and pyrite; the pyrite is also observed in hand specimens (Kepferle and others, 1985; Provo and others, 1978). The sample was collected from a fresh road cut along U.S. Highway 64, about 8 mi west of Morehead, Rowan County, Ky., at lat 38°09′56″N., long 83°35′38″W. (Kepferle and others, 1985).

A preliminary report (Kepferle and others, 1985) proposed elemental concentrations based on a limited data base. Recommended concentrations published since then (Kane and others, 1990) (table 1) were derived from a larger data set that included the original Eastern Gas Shale Project data, the International Geological Congress (IGC) Metalliferous Black Shales (#254) Project, and concurrent contributions from USGS and other laboratories.

This report contains details of the statistical treatment used for derivation of recommended concentrations from the collected data. That treatment, published previously (Kane and others, 1990), is summarized in table 2. This report also contains conclusions as to analytical method(s) of choice for individual elements and presents some of the more accurate methods used in the collaborative analytical programs leading to recommended concentrations for the material. Some of these methods (for example, Spies and others (chap. B, this vol.) and Roelandts (chap. C, this vol.)) are routine procedures applied without any necessary modifications due to the unique sample matrix. Other methods (for example, Wandless (chap. D, this vol.) and Huka and Rubeska (chap. E, this vol.)) require nonroutine application to obtain accurate analyses of SDO–1. The shale is the most sulfur-rich and the most organic-rich of any samples in the USGS GRS suite. The high sulfur and organic carbon contents of the material presented unique analytical problems affecting the accuracy or trueness of analysis. The analytical methods are presented here in order to assist laboratories in improving their procedures for shale analysis.

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Table 1. Summary of constituent concentrations for USGS Devonian Ohio Shale SDO–1

	Recommended: weight percent in sample, as received		Recommended: μg/g in sample, as received		
SiO_2	49.28±0.63	As	68.5±8.6	Ni	99.5±9.9
Al_2O_3	12.27±0.23	Ba	397±38	Pr	8.9±0.66
Fe_2O_3 TOT	9.34±0.21	Ce	79.3±7.8	Rb	126±3.9
CaO	1.05±0.047	Co	46.8±6.3	Sc	13.2±1.5
MgO	1.54±0.038	Cr	66.4±7.6	Sm	7.7±0.81
Na_2O	.38±0.026	Dy	6.0±0.65	Sr	75.1±11.0
K_2O	3.35±0.061	Eu	1.6±0.22	U	48.8±6.5
P_2O_5	.11±0.007	Ga	16.8±1.8	V	160±21
TiO_2	.71±0.031	La	38.5±4.4	Y	40.6±6.5
MnO	.042±0.005	Mo	134±21	Yb	3.4±0.46
		Nb	11.4±1.2	Zn	64.1±6.9
		Nd	36.6±3.3	Zr	165±24
	Average: weight percent in sample, as received		Average: μg/g in sample, as received		Range: μg/g in sample, as received
LOI	21.7±0.90	B	128±11	Ag	0.094–0.17
S	5.35±0.44	Be	3.3±0.57	Au	.002–0.0035
CO_2	1.01±0.21	Cs	6.9±1.2	Bi	2–<10
C_{TOT}	9.95±0.44	Cu	60.2±9.6	Br	5
C_{org} (measured)	(range 8.98–10.4)	Er	3.6±0.55	Cd	<2–<10
C_{org} (calculated)	9.68±0.45	F	697±88.5	Ge	1.3
H_2O^- (moisture)	1.21±0.50	Gd	7.4±1.9	In	<0.2
H_{TOT}	1.34±0.06	Hf	4.7±0.75	Sb	4.1–4.8
N_{TOT}	.347±0.043	Hg	.19±0.08	Se	1.9–6.8
		Ho	1.2±0.11	Ti	8.3
		Li	28.6±5.5	W	3.3
		Lu	.54±0.14		
		Pb	27.9±5.2		
		Sn	3.7±1.2		
		Ta	1.1±0.13		
		Tb	1.2±0.24		
		Tm	.45±0.08		

Table 2. Statistical treatment of compiled data (Kane and others, 1990, and references therein; also chap. A, this vol.)

1. Assess normalcy of data distribution of laboratory results (each of which are the average of several replicate analyses) and iteratively reject as gross outliers the individual data that lead to significant deviation from normalcy at the 95 percent confidence level.

   tests:
   a. Arithmetic mean and median are approximately equal;
   b. Distribution is neither skewed nor kurtopic; and
   c. Chi-square and (or) Kolmogorov-Smirnov tests indicate normalcy.

2. Calculate mean and standard deviation for compiled data after gross outlier rejection; convert standard deviation to relative standard deviation (rsd). If rsd is 2 percent for major elements, between 5 and 10 percent for minors, or 15 percent for trace elements, proceed to step 4.

3. Test extreme individual laboratory average data against the compiled data mean $\overline{X}$ calculated in step 2 by means of a two-sided t–test. Reject any data shown to differ significantly at the 95-percent confidence level from $\overline{X}$. Repeat steps 1 and 2 until no further rejection is indicated.

4. Group laboratory average data surviving the rejection procedure by analytical method. Perform a one-way analysis of variance with method as the classification variable; determine significance of intermethod differences at the 95-percent confidence level.

5a. Recommend concentrations of oxide/element (1) if the final iterated $\overline{X}$ is based on at least five laboratory data determined by at least three independent methods showing no significant method differences and (2) if the rsd of $\overline{X}$ meets step 2 criteria.

5b. Cite the final iterated $\overline{X}$ as the average concentration of the oxide/element if it is based on at least five laboratory data but in some other aspect does not meet the criteria in 5a for a recommended concentration. Cite only a concentration range if there are fewer than five laboratory data after rejection steps 1–3.

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Chapter A

Statistical Treatment of Contributed Data in the Derivation of Recommended Concentrations for Devonian Ohio Shale SDO-1

By JEAN S. KANE

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THE USGS REFERENCE SAMPLE DEVONIAN OHIO SHALE SDO-1

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Statistical Treatment of Contributed Data in the Derivation of Recommended Concentrations for Devonian Ohio Shale SDO–1

By Jean S. Kane

Abstract

This report presents details of the statistical procedures used to derive recommended concentrations for the U.S. Geological Survey reference shale SDO–1 from data contributed by many U.S. Geological Survey and other geochemical laboratories. These include analysis of variance both to evaluate material homogeneity and to assess the significance of differences in constituent analyses between laboratories and (or) methods of analysis. Also included is a review of analytical methods used for individual elements, with evaluation of which one(s) are most accurate and precise and which are most subject to potential systematic error.

INTRODUCTION

The U.S. Geological Survey (USGS) geochemical reference sample (GRS) Devonian Ohio Shale SDO–1 (note that a Russian reference sediment sample is also called SDO–1) was first introduced as a control sample in conjunction with the Eastern Gas Shale program, 1976–1981. Publications of analytical results from that program (Leventhal and others, 1978; Department of Energy, 1978) and tentative recommended concentrations (Kepferle and others, 1985) have been followed by a number of reports (for example, Frost and others, 1985; Coveney and Glascock, 1989; Kane and others, 1990; Leventhal and Knapp, 1988) that indicate the continued geochemical interest in metalliferous black shales. One of these (Kane and others, 1990) presented recommended concentrations and their uncertainties for 40 elements, based on contributed data from more than 50 laboratories worldwide.

Analytical laboratories providing analyses for metalliferous black shale geochemical studies require an appropriately matrix-matched GRS to validate analytical methods and otherwise ensure analytical accuracy. A review of the collaborative data base for Devonian Ohio Shale SDO–1 (Kane and others, 1990) indicates that although many laboratories are performing analyses with the required accuracy on SDO–1 (and presumably on metalliferous black shales, in general), some are experiencing difficulty with accurate analyses of one or several elements in samples of this type. This report examines the total data base with a view to identifying the method(s) of choice for a given element. The identification will be based on those methods showing the highest within-laboratory precision, the best between-laboratory repeatability, and lowest rejection rates in the process of deriving recommended concentrations, following the iterative procedure outlined in Kane and others (1990).

BETWEEN-BOTTLE VARIANCES

We begin the discussion with a review of the between-bottle analysis of variance (anova) presented in Kane and others (1990). Mineralogically, SDO–1 has three principal components (clay, pyrite, and organic matter) that differ considerably in density and composition. Sampling errors can be highly significant in the analyses of such mixtures. The ability to detect sampling error between bottles is a function of measurement precision for within-bottle subsamples (Kane, 1992). It is the latter which Ingamells illustrates for Cr in G–1 (Ingamells and Pitard, 1986). In this example, the within-bottle subsampling error results for the trace element Cr because it occurs at a very high concentration in the mineral chromite but at a much lower concentration in the bulk sample. The anorthite-/orthoclase mixture described in Ingamells and Pitard (1986) demonstrates that within-bottle subsampling errors can still be significant even though much less pronounced for mixtures of major mineral phases than for dispersed minerals in bulk sample.

The basic homogeneity study for a reference sample looks primarily at sampling variance between bottles or between units-of-issue for the GRS. For SDO–1, significant bottle variances for several major oxides were found by and many collaborating laboratories (Kane and others, 1990),

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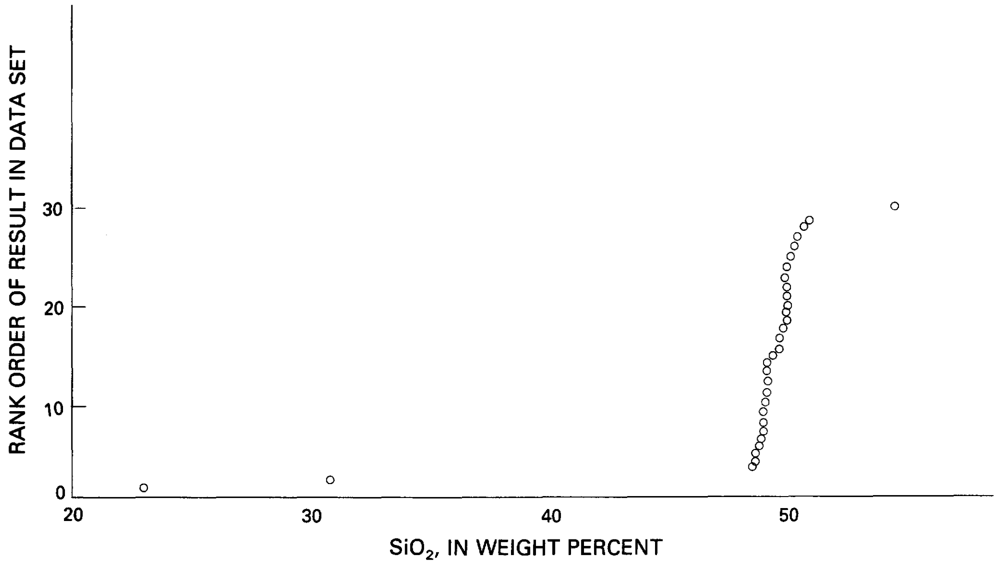

Figure 1. S-curve showing distribution of SiO_2 results for SDO–1.

the between-bottle variances identified amounted to 90 percent or more of the total laboratory variance for several of those laboratories. Furthermore, these between-bottle variances appear to account for roughly 50 percent of the between-laboratory variances for the total data set, which amounted to 1-percent relative standard deviations (rsd's) for SiO_2, Al_2O_3, and Fe_2O_{3T} and to about a 10 percent rsd for loss on ignition (LOI).

The trace elements associated with a particular principal mineral component should be expected to exhibit bottle variances parallel to those for the major oxides comprising that mineral fraction. Thus, between-bottle subsampling error would be expected to occur for Cu and other chalcophile trace elements associated with the pyrite phase in SDO–1 as well as for iron. However, the occurrence of within-bottle sampling variance would degrade the ability to detect between-bottle sampling variance in the same way as would the use of a relatively imprecise analytical method (Kane, 1992). None of the chalcophile trace elements were found to be heterogeneously distributed between bottles. However, many had larger standard deviations of measurement in the compiled data set than expected for the concentrations at which they occurred, presumably because of a large within-bottle subsampling component of variance. Similarly, the rare earth elements (REE's), expected to be distributed in the same manner as the clays, do not show the between-bottle variances noted for Al and Si. Although uranium and molybdenum, whose distributions should parallel the organic matter, are not measurably heterogeneous between bottles, LOI is heterogeneous. Therefore, sampling is thought to be a major factor in the uncertainty of compiled data averages for these elements.

TESTS TO IDENTIFY OUTLIERS FOR REJECTION

Despite the reality of a significant sampling component in the between-laboratory/method analysis of variance for some elements, what follows will neglect that subsampling error. We will instead attempt to discern the other causes of interlaboratory and intermethod disagreements, and focus on those.

Distribution of the Data

The iterative process by which contributed data are accepted or rejected begins with an evaluation of the normalcy of the distribution of submitted data. Assuming that no bias affects any contributed data, but that all error is truly random, the contributed data should have a normal distribution (Deming, 1943; Youden, 1960). Several measures of normalcy of the distribution can be made, each having limitations related to the size of the data set. These measures are the agreement between the arithmetic mean and the median, the coefficients of skewness ($\sqrt{b_1}$) and of kurtosis (b_2), chi-square (X^2) and the Kolmogorov-Smirnov maximum deviation (D) (Dixon and Massey, 1983; Lister, 1982; Deming, 1943; Siegel, 1956). The data for SiO_2 before any rejection is both negatively skewed and leptokurtic. The mean and median differ in the second significant figure, and the standard deviation of the mean indicates that error begins in the third significant figure. Both X^2 and D indicate less than 1-percent probability of the distribution being normal. Visual inspection of a simple S-curve distribution of the data (fig. 1) readily reveals the outliers to be the two lowest and one highest compiled values. With their removal, all measures of goodness of fit indicate that the distribution is normal. The mean and median now differ

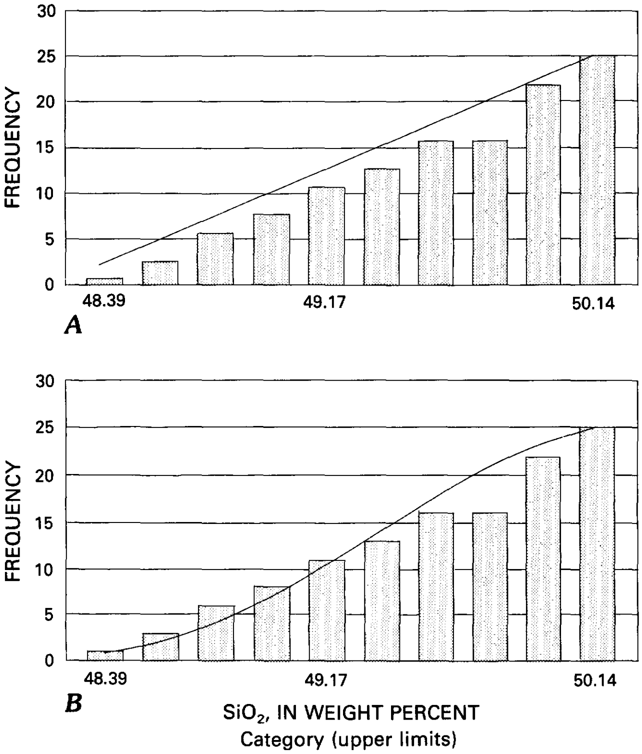

Figure 2. Fit of data (cumulative frequency) to (*A*) theoretical Chi-square distribution and (*B*) to normal distribution.

only in the fourth significant figure. The fit of the data to theoretical X^2 and normal distributions are shown in figures 2*A*, 2*B*.

t–Test for Comparison of Individual Laboratory Results With the Overall Mean

Once the data distribution is normal, the high and jlow individual laboratory averages ($\overline{X}_i$) are compared to the iterated mean ($\overline{X}_T$) using a *t*–test (Dixon and Massey, 1983; Lister, 1982). This rejection procedure can be overly severe when n is large, and inadequately rigorous when n is small. For example, at $n=30$ rejection occurs at $|\overline{X}_i-\overline{X}_T|=0.5s$, but at $n=3$ it occurs at $|\overline{X}_i-\overline{X}_T|=3s$, where s is the standard deviation of $\overline{X}_T$. Particularly in view of the bottle inhomogeneities already noted, excessive rejection must be avoided to arrive at realistic uncertainty estimations for the recommended concentrations.

Returning to the SiO$_2$ data set, once the data distribution was normal after eliminating the two lowest and one highest results, the interlaboratory mean had an rsd of 1.3 percent, within the criteria range for a recommended major-oxide concentration. *t*–test criteria for $n=27$ would reject individual laboratory results deviating from the overall average by only 0.56s, but this value approaches the bottle-to-bottle variation identified in the homogeneity study. Several successive iterations based on the *t*–test criteria have little to no effect on either the final mean or the final uncertainty of that value (49.28±0.63 percent at $n=27$, rsd 1.3; 49.27±0.49 percent at $n=19$, rsd 1.0). *t*–test rejection is therefore not carried out. Instead, method analysis of variance is performed, as discussed in the next section, and the value of 49.28±0.63 percent is recommended for SiO$_2$ in SDO–1.

The Ba data set will illustrate the case where all parameters, with the possible exception of X^2, showed the initial distribution to be normal. No data were rejected through data distribution tests, but six laboratory results were rejected based on *t*–tests. The procedure and results are shown in table 1. The initial $\overline{X}_T$ for Ba is 440±117 μg/g for $n=26$. Despite normalcy of the distribution, the uncertainty of the interlaboratory average (rsd 27 percent) is unacceptably large. *t*–test rejection occurred pairwise for the high and low extreme values, which differed by more than 0.56s (66 μg/g) from $\overline{X}_T$. Iteration gave a new $\overline{X}_T$ of 437±93 μg/g for $n=24$. At this point, reevaluation of the distribution indicated deterioration; all parameters were closer than initially to critical values at which the hypotheses of normal distribution would be rejected. Additionally, the magnitude of the rsd (22 percent) required further rejection. After the next two cycles of pairwise *t*–testing that led to one-sided rejection of high values, skewness was serious, X^2 also indicated that the distribution was not normal, and the rsd (18 percent) was still too large to permit recommending the interlaboratory average Ba concentration of 419 μg/g. Three further *t*–test iteration cycles, again rejecting only high values, led to $\overline{X}_T$=394±37 μg/g for $n=19$. Iteration was then suspended since the distribution was then normal under all tests, and the rsd of 9.4 percent met procedural criteria.

Between-Method Variance

Intermethod agreement, the final criterion for recommending an elemental concentration, parallels the National Institute of Standards and Technology (NIST) certification procedures (Uriano and Gravatt, 1977; Natrella, 1963; Cali and Reed, 1974; Michaelis, 1975), which require between-method agreement for the certification of concentrations in standard reference materials (SRM's). These certified concentrations represent the closest possible estimation of "true value," an ideal that all analyses attempt to approach but nonetheless remains unknown (Youden, 1960; International Organization for Standardization (ISO), 1978, 1989). We accept the hypothesis that method averages are the same when that is true at the 95 percent confidence level, that is, when there is ≤5 percent probability that the method averages are statistically different.

In the SDO–1 and most other compiled data bases, significant between-laboratory variances are the rule, not the exception, where data permits their evaluation. This variance is not entirely unexpected (Youden, 1960;

Table 1. Step-by-step iteration of SDO–1 Ba recommended concentration in μg/g

[rds, relative standard deviation; NS, not significant; (S), significant at 95%, but not at 99%, confidence level; S, significant at both 95% and 99% confidence level]

Mean and standard deviation (rsd)	Number using: Data	Test for normal distribution					Decision/comment
		Median	Skewness	Kurtosis	Kolmogorov-Smirnov (D) (Probability dist. is normal)	Chi-square (X^2) (Probability dist. is normal)	
440±117 (27%)	26	406	NS	NS	0.227 (0.14)	15.48 (0.000)	Four of five tests show distribution normal; however, rsd exceeds limit, and *t*–test of extreme high and low values leads to their rejection.
428±102 (24%)	25	404	NS	NS	.205 (.247)	14.04 (.000)	
437±94 (22%)	24	406	(S)	NS	.263 (.063)	12.08 (.007)	rsd still unacceptable and distribution deteriorating; continue *t*–test rejection.
428±85 (20%)	23	404	S	NS	.255 (.098)	8.77 (.032)	
419±74 (18%)	22	401	S	NS	.228 (.202)	6.91 (.032)	Rejection is one-sided (high values only) at this point; skewness is significant; with each new rejection, D and X^2 show increasing probability that distribution is normal.
419±63 (15%)	21	399	S	NS	.193 (.413)	5.05 (.080)	
401±47 (12%)	20	394	NS	NS	.117 (.946)	2.86 (.240)	Rsd remains unacceptable until skewness is removed. *t*–test indicates unacceptability of high value.
394±37 (9.4%)	19	388	NS	NS	.088 (.998)	.249 (.618)	At $n=19$, rsd=9.4 percent and distribution is normal. Criteria to recommend concentration are met.
398±33 (8.3%)	18	394	NS	NS			*t*–tests indicate further rejection, but iterated concentrations change only slightly; further iteration is unwarranted.
394±29 (7.4%)	17	388	NS	NS			

Bastenaire, 1979), as subtle bias is likely to affect even the most carefully developed and applied analytical method. Interlaboratory differences are evaluated with a standard anova procedure using laboratory rather than bottle as the classification variable. Complete evaluation requires that all contributing laboratories submit individual analytical results, and not just laboratory averages, so that within-laboratory or within-method variance can be calculated.

Although 11 laboratory averages for SiO_2 based on X-ray fluorescence (XRF) analysis survived the iterative rejection process, only four of those laboratories reported individual results in addition to the final laboratory average. For those four laboratories, the between-laboratory anova shows highly significant differences, as seen in table 2. Similarly, three laboratories using some variation of the Shapiro and Brannock (1962) "rapid rock" procedure obtained significantly different results. The same is true for three other laboratories using inductively coupled plasma–atomic emission spectrometry (ICP–AES) after an unspecified decomposition and for two laboratories using colorimetry (table 2).

However, when method rather than laboratory becomes the classification variable and interlaboratory method averages are compared, no significant differences are found. The method averages for SiO_2, based on XRF ($n=11$), colorimetric ($n=2$), dc arc AES ($n=1$), and "rapid rock" ($n=3$) analyses, are the same, with >95-percent probability, as shown in table 3. The intermethod average of 49.28±0.63 percent SiO_2 is designated a recommended concentration because both the intermethod agreement and the magnitude of the interlaboratory relative standard deviation (rsd) meet USGS criteria for recommended concentrations (Kane and others, 1990). Again, we point out that roughly half of the final interlaboratory rsd is due to bottle differences.

A similar evaluation process led to recommended concentrations for all rock-forming major oxides measured in SDO–1. For most major oxides other than SiO_2, the iteration proceeded through several cycles, removing either a single point or paired high and low outliers as appropriate, before resulting in an acceptable, normal data distribution.

For the Ba data set, five methods of analysis were also used by contributing laboratories; the anova procedure resulted in an 82 percent probability that results from all five methods were the same. Therefore, the Ba concentration was also recommended.

Similarly, concentrations were recommended for 23 other trace elements based on the outlined procedure.

Table 2. Between-laboratory analysis of variance: SiO_2 in weight percent

Method/ laboratory		Laboratory mean and standard deviation	Degrees of freedom	F-ratio[1]	Probability laboratory means do not differ
XRF	2	48.43±0.59	4,21	29.72	0.0000
	5	50.05±0.09			
	6	48.57±0.52			
	15	50.16±0.077			
	17	49.54±0.067			
Fusion ICP-AES	1	50.05±0.12	2,11	93.53	.0000
	4	48.68±0.22			
	16	48.77±0.23			
Color	14	49.45±0.16	1,10	51.04	.0001
	15	48.73±0.17			

[1] F-ratio=$\frac{\text{variance between laboratories}}{\text{variance within laboratories}}$

Table 3. Between-method analysis of variance anova: SiO_2

Method	Method mean and standard deviation	Number of laboratories using method	Anova data
XRF	49.12±0.47	11	Degrees of freedom=3,13
Fusion ICP-AES	49.29±0.71	3	
Color	48.97±0.39	2	F-ratio=0.115
dc arc AES	49.22	1	Probability method means do not differ=0.97

Average values, which did not meet criteria for recommended values, were derived for LOI, moisture, CO_2, C_{org}, C_{TOT}, and 16 trace elements.

Alternative Identification of Outliers Based on Quality-Control Practices

Rejection of data could be more appropriately based on quality- control (QC) evidence rather than statistical tests by referencing a method standard operating procedure (SOP). For example, if the SOP reported that the routinely achievable accuracy of the method did not meet the criteria for recommended concentrations, data obtained using the procedure would be rejected. QC evidence could also be provided by reporting accurate data for an appropriate, previously characterized reference sample. Since neither option was available in characterizing SDO–1, statistical procedures alone were relied on in determining which data to reject or accept in the final data set.

Ba data provides an excellent illustration of the desirability of QC criteria for rejection. In another paper in this volume (chap. D), Wandless discusses the large interference that U can cause in the Ba result in instrumental neutron activation analysis (INAA). In fact, several of the rejected high values in the data set were INAA values; the correction indicated in the Wandless paper would bring all rejected values within the uncertainty of the recommended concentration. SOP's from each of the contributing laboratories would be required, however, to identify whether or not this factor actually explained the high INAA results that were rejected. Acid decomposition prior to ICP–AES might be expected to result in low Ba results, or at least to more within-method variation than in a fusion data set, because of sulfur oxidation to sulfate and potential precipitation of Ba during the decomposition. The QC approach allows the underlying causes of poor data to be identified and, thus, permits correction of procedures to eliminate the error. Statistical procedures alone do not accomplish this aim.

It is not always obvious how best to identify methods. The original rapid-rock procedure (Shapiro and Brannock, 1962) used several single-element colorimetric or flame atomic absorption determinations after a fusion decomposition of the sample; today, ICP–AES substitutes for most of those other final measurements. Is a single, broad method specification of rapid rock sufficient for all of these variations? ICP–AES preceded by acid decomposition is in some ways distinctly different from ICP–AES preceded by fusion decomposition, but in other ways the two are identical. ICP–AES and dc arc AES are distinctly different in that one analyzes sample after decomposition and the other analyzes sample without prior decomposition. The two methods have different excitation mechanisms, and excitation occurs at different temperatures, but in the final analysis both are based on the single atomic emission principle. We have used rather broad classifications rather than extremely narrow ones, while maintaining a distinction between solid sample and solution analysis.

Ideally, at least three methods of analysis have been used to analyze both solid and decomposed sample, and the methods differ in broad classification: X-ray spectrometry, atomic (absorption/ emission) spectrometry, instrumental neutron activation analysis, mass spectrometry, classical wet chemistry, and others. With few exceptions, most

Table 4. Summary of major oxide analyses by method
[( ), reported, but rejected; leaders (—), none reported]

Total number of data accepted	Oxide	Number of accepted analyses that were determined by:						
		WDXR	Fusion ICP–AES	Unknown decomp ICP–AES	INAA	AAS	dc arc AES	Color
26	SiO_2	11	3	2	—	—	1	1
23	Al_2O_3	11	2	6	( )	4	( )	1
26	Fe_2O_{3TOT}*	10	3	5	2	4	2	( )
24	MgO	8	3	4	( )	4	1	—
27	CaO	10	3	4	( )	3	1	—
24	Na_2O	7	3	4	3	3	2	—
22	K_2O	10	3	3	2	3	( )	—
25	TiO_2	10	3	3	( )	( )	—	1
20	P_2O_5	8	2	5	( )	( )	( )	1
22	MnO	7	3	6	( )	4	2	( )

	Number of rejected analyses that were determined by:						
	WDXR	Fusion ICP–AES	Unknown decomp ICP–AES	INAA	AAS	dc arc AES	Color
SiO_2	0	0	0	—	—	1	1
Al_2O_3	2	1	1	2	1	1	1
Fe_2O_{3TOT}*	0	0	0	3	1	0	1
MgO	1	0	2	1	0	0	—
CaO	0	0	2	1	0	1	—
Na_2O	3	0	1	0	1	0	—
K_2O	0	0	2	1	0	2	—
TiO_2	0	0	0	2	—	—	0
P_2O_5	1	1	1	—	—	—	0
MnO	1	0	0	—	0	0	—
$100\times\frac{\text{total number rejected for method}}{\text{total number accepted for method}}$	9%	7%	24%	140%	12%	78%	75%

*Total iron reported as Fe_2O_3; occurs as FeS_2, $FeCO_3$ or FeO (Leventhal and Hosterman, 1982)

notably LOI and H_2O (tot), this goal is readily achievable for major oxides but much more difficult to achieve for trace constituents, as will be seen shortly.

FREQUENCY OF USE AND ACCURACY OF METHODS USED BY LABORATORIES IN SDO–1 ANALYSIS

Based on the method averages from which recommended concentrations were derived, we can draw conclusions as to (1) frequency of use, or popularity, of specific methods and (2) general acceptability of each of those methods in terms of accuracy and precision (or in ISO (1978) terminology, trueness and repeatability) for each constituent measured. Based on the percentage of laboratory averages obtained by any acceptable method that had to be rejected during the iteration leading to the recommended concentration, some conclusion regarding ease of application or trouble-free nature of the method can also be drawn. We now examine the compiled data with respect to these conclusions. In doing so we must note that a sizeable number of laboratories did not specify the method of analysis used.

Major Oxides

Approximately 70 percent of the laboratories reporting data specified the analytical method used; from that specification, it was determined that X-ray fluorescence and atomic spectrometry provided the bulk of the major constituent data, as shown in table 4. Most laboratories using XRF for these analyses used the wavelength-dispersive method (WDXRF) and fused the samples into glass beads or discs prior to X-ray excitation, as described, for example, by Spies and others (chap. B, this vol.). Energy-dispersive X-ray analysis of pressed powder (EDXRF) was used by only one laboratory (Kopp and Furman, chap. G, this vol.). The standard protocol developed for clays and soils in Kopp's laboratory was inadequate in correcting for the shale matrix effects encountered in analyzing SDO–1 (Kopp and Furman, chap. G, this vol.). Since less than 10 percent of all WDXRF data in the compilation was rejected during the iterative process leading to recommended concentrations, it can be concluded that the WDXRF method is highly repeatable between laboratories and readily applied with accuracy to samples of the shale matrix. The method is particularly advantageous because it permits determination of sulfur along with other major constituents. During ignition prior to fusion, most sulfur is lost, but some is retained in ignited sample (Kane and Skeen, chap. F, this vol.). Measurement of both retained sulfur in ash and LOI is important if oxide summations are used to assess acceptability of the analysis. However, the nature of the shale sample introduces considerably more error in the oxide summation evaluation than that which occurs for typical igneous rocks (Lechler and Desilets, 1987), as discussed elsewhere in this volume (Kane and Skeen, chap. F, this vol.; Huka and Rubeska, chap. E, this vol.). Also, it must be recognized that the reporting of total iron as ferric oxide, following normal rock analysis convention, accurately reflects the iron occurrence in the ignited and fused XRF analytical sample, but not in the shale itself (Leventhal and Hosterman, 1982). This reporting convention also affects the oxide summation of the recommended concentrations for the reference sample itself, although not for the ignited residue that is analyzed by XRF.

Atomic spectrometry can be subdivided into emission (AES) and absorption (AAS) spectrometries, and each of these can be subdivided as well. For example, subdivision of AES by excitation process would result in inductively coupled plasma (ICP–AES), direct current plasma (DCP–AES), and dc arc AES methods. In this work, each was treated as a different method for the method anova statistics. Also, both AES and AAS could be subdivided depending on whether or not prior sample decomposition was required for analysis, leading to solid/flux, acid decomposition, fusion decomposition categories for the method anova. Although this subdivision led to several distinct atomic spectrometric methods for method anova, intermethod agreement was not considered sufficient for purposes of recommending concentrations if all methods were fundamentally atomic spectrometric methods. A totally independent method, for example, XRF, INAA, or gravimetry, in agreement with the atomic spectrometric methods, was required. Based on low rejection rates indicating overall accuracy of submitted data, fusion ICP–AES is a method of choice for major constituents; within-laboratory precision for some oxides is slightly poorer than for WDXRF, and S cannot be included in the analysis; but otherwise the two methods are equally suited to accurate and precise characterization of reference samples for their major constituents.

Acid (or unspecified) decomposition ICP–AES and acid decomposition AAS were also applied successfully to SDO–1 analysis, as was flame photometry for Na and K. The obvious disadvantage of any analysis following acid decomposition is the inability to provide SiO_2 results. For some major constituents, chemical methods including colorimetry, volumetric analysis, and gravimetry were used by a small number of contributors, as were INAA analyses. Combustion/coulometry was the primary method for carbon and sulfur analyses. Chemical analyses and INAA, neither of which show the robustness between laboratories of WDXRF and atomic spectrometry, were used less frequently and had higher rejection rates and larger between-laboratory rsds for data surviving the rejection process than the optimum methods.

Trace Elements

Intermethod comparisons of trace element determinations are more difficult to generalize than those for major oxides. A wider range of methods are used, but the extent of overlapping coverage of specific elemental suites between methods is much more limited, as indicated in table 5. For example, INAA is used to provide a sizeable portion of the REE data; XRF analyses are also used extensively to provide Ce and La analyses, but no other REE data. However, direct ICP–AES without prior group separations and AAS are seldom used to provide any REE data. On the other hand, those atomic spectroscopic methods provide a major portion of data for such elements as Cu, Li, and Pb where INAA data are totally absent. Confirmation of values by several independent techniques was readily achieved for the major oxides but much harder to accomplish for the traces. Also, the data sets for each trace element were generally smaller (average n=9) than those for the majors (average n=20) except in a relatively few instances. We have already examined the intermethod Ba data in detail, while discussing the rejection process and recommended value derivation. We now will look at a number of other trace elements in similar detail.

Although INAA methods historically dominated in the determination of REE, IDMS has long been considered the method of choice for the odd atomic weight REE. However, even in data bases for reference samples like BCR–1 and BHVO–1 used throughout the U.S. space program, the number of IDMS data points available have represented only a small fraction (18 percent for BCR–1 and 5 percent for BHVO–1) of the total data set (Flanagan, 1976; Gladney and others, 1983). More recently, both ICP–AES following group separation and ICP–MS methods have been developed for the REE, making intermethod validation of REE recommended concentrations possible. Table 6 shows that no clear superiority of one method over the others results from F-tests comparing method variances or *t*–tests comparing the several method averages to one another for most of the REE. Larger data sets, however, would improve the rigor of the tests and might show subtle differences between methods results that are not statistically significant in the current data set. A case in point is Ce, for

Table 5. Summary of trace element analyses by method

[leaders (—), none reported by that method; sepn., separation]

Elements whose concentrations were recommended	Number of accepted (rejected) analyses that were determined by:											
			ICP–AES		AAS				Other			
	XRF	INAA	Direct	Sepn. prior	Flame	Hydride or CV	HGA	Dc arc AES	ICP–MS	DCP	Color	DNA
As	1(1)	3(0)	3(1)	—	—	0(1)	3(1)	—	—	—	—	—
Ba	8(1)	1(3)	6(2)	—	1(0)	—	—	3(4)	—	—	—	—
Ce	7(0)	5(1)	3(3)	5(1)	—	—	—	3(0)	1(0)	—	—	—
Co	3(0)	5(1)	7(0)	—	—	—	3(1)	—	—	—	—	—
Cr	6(2)	6(0)	8(0)	—	—	—	—	5(1)	—	1(0)	—	—
Dy	—	2(0)	—	6(2)	—	—	—	—	1(0)	—	—	—
Eu	—	6(1)	1(2)	7(1)	—	—	—	—	1(0)	—	—	—
Ga	2(0)	—	3(8)	—	—	—	0(1)	5(0)	—	—	—	—
La	5(2)	7(0)	7(0)	5(0)	—	—	—	5(1)	1(0)	—	—	—
Mo	3(1)	3(0)	7(1)	—	—	—	—	4(1)	—	—	—	—
Nb	6(3)	—	4(2)	—	—	—	—	1(1)	—	—	—	—
Nd	1(0)	7(0)	3(0)	7(0)	—	—	—	1(0)	1(0)	—	—	—
Ni	8(1)	2(0)	6(1)	—	4(2)	—	1(0)	6(0)	—	1(0)	—	—
Pr	1(0)	—	0(1)	6(0)	—	—	—	—	1(0)	—	—	—
Rb	7(1)	3(2)	1(0)	—	—	—	—	0(1)	—	—	—	—
Sc	1(0)	4(1)	7(0)	1(0)	—	—	—	4(0)	1(0)	—	—	—
Sm	—	6(1)	1(1)	7(0)	—	—	—	—	1(0)	—	—	—
Sr	9(0)	0(1)	7(0)	—	—	—	—	3(5)	—	—	—	—
U	1(1)	8(1)	2(1)	—	—	—	—	—	—	—	—	1(0)
V	4(0)	1(0)	9(0)	—	—	—	—	5(1)	—	1(0)	1(0)	—
Y	9(1)	—	5(4)	2(2)	—	—	—	3(3)	—	—	—	—
Yb	—	6(0)	4(0)	6(1)	—	—	—	0(3)	1(0)	—	—	—
Zn	7(0)	2(1)	6(0)	—	5(0)	—	—	3(2)	—	1(0)	—	—
Zr	9(0)	0(2)	3(1)	—	—	—	—	5(1)	—	—	—	—
Elements whose concentrations were reported as average												
B	—	—	0(1)	—	—	—	—	5(1)	—	1(0)	—	—
Be	—	—	5(1)	—	—	—	1(0)	3(2)	—	0(1)	—	—
Cs	1(0)	6(1)	—	—	—	—	—	—	—	—	0(1)	—
Cu	6(1)	—	8(0)	—	6(0)	—	—	5(1)	—	1(0)	—	—
Er	—	—	0(1)	7(0)	—	—	—	—	1(0)	—	—	—
Gd	—	2(0)	0(1)	6(2)	—	—	—	—	1(0)	—	—	—
Hf	1(0)	7(0)	—	—	—	—	—	—	—	—	—	—
Ho	—	—	0(2)	6(0)	—	—	—	—	1(0)	—	—	—
Li	—	—	5(0)	—	1(0)	—	—	0(2)	—	—	—	—
Lu	—	7(0)	0(1)	8(0)	—	—	—	—	1(0)	—	—	—
Pb	2(0)	—	4(0)	—	5(0)	—	—	5(2)	—	1(0)	—	—
Sn	2(2)	—	0(2)	—	—	—	—	2(2)	—	—	—	—
Ta	0(2)	6(0)	0(2)	—	—	—	—	—	—	—	—	—
Tb	—	7(0)	0(1)	6(0)	—	—	—	—	1(0)	—	—	—
Th	—	5(1)	—	—	—	—	—	—	—	—	—	—
Tm	—	2(0)	—	5(0)	—	—	—	1(0)	1(0)	—	—	—

which the individual method ranges are plotted in figure 3. Apparently, solution methods (ICP–AES, with and without separation, and ICP–MS) produce results that are slightly lower than solid-sample methods (INAA, XRF, dc arc AES). Ce is known to occur in minerals resistant to acid attack, which was used almost exclusively in obtaining the solution-method results. Results from all six methods are the same, having a 33-percent probability; however, the probabilities increase to 55 percent and 88 percent, looking for agreement between either the solution (ICP–AES, ICP–MS) or the solid-sample methods (dc arc AES, XRF, INAA).

In deriving the recommended concentration for As, the last iteration acceptance range was 52–84 μg/g. Intermethod agreement exists with a probability of only 3 percent between XRF, ICP–AES, INAA, and hydride

Table 6. Selected rare earth elements: Comparison of results in μg/g from INAA, ICP–AES after separation, ICP–MS methods

[S, significant at 95% confidence; NS, not significance at 95% confidence]

Element	INAA	Ion exch. Sepn. ICP–AES	ICP– MS	Anova* for differences in precision	*t*–Test for differences in means
Ce	78.1±6.1	74.0±2.8	73.2±1	NS	NS
Nd	36.6±3.2	37.4±1.6	7.0	NS	NS
Sm	7.8±0.40	7.8±0.81	6.8	NS	NS
Eu	1.74±0.18	1.65±0.23	1.71	NS	NS
Gd	7.82±0.78	6.55±0.49	6.9	NS	NS
Tb	1.07±0.19	1.28±0.19	.80	NS	NS
Lu	.63±0.16	.45±0.02	.42	NS	NS

*Omits ICP–MS

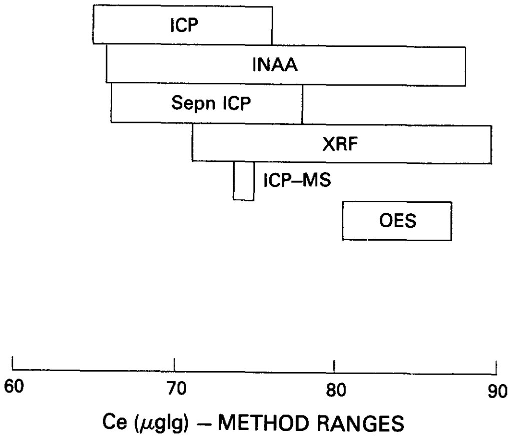

Figure 3. Ce data ranges for each method of analysis.

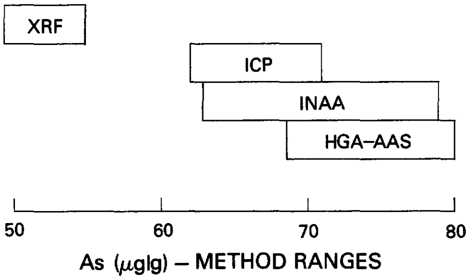

Figure 4. As data ranges for each method of analysis.

generation-AAS method means, but within each method group between-laboratory relative standard deviations of approximately 10 percent are found. If, we plot the full range of As data before rejection by method (fig. 4), we would intuitively reject the XRF method as providing data which differs from that for the other three methods. Repeating the between-method anova after removing the one XRF result previously retained reveals that the probability that the three method averages from ICP–AES, INAA, and hydride-AAS are the same improves considerably, to 43 percent. Although two methods require sample dissolution, one does not, which suggests no decomposition error. Two totally different classes of method, atomic spectrometry and nuclear, are in agreement. The intermethod average can therefore be recommended, having fair confidence that no method-specific error source is affecting its reliability.

On the other hand, few of the individual laboratory results for As agree with one another if the anova is performed between laboratories rather than between methods, as discussed earlier. A considerable part of the discrepancy is probably attributable to calibration protocol differences. INAA and XRF in particular are often calibrated with secondary standards, and uncertainties in the calibration standard values can be a significant factor in the overall analytical error for each laboratory. A notable absence of hydride generation data for the sample suggests difficulties with that method in analyzing organic-rich (and (or) sulfur-rich) samples. One late addition to the data set, in fact, was a hydride generation As result of 38 μg/g, the lowest result submitted. There is some indication that the observed bias may be due to the presence of As in an organo-metallic complex that does not decompose under the conditions used to prepare samples for hydride generation (A. Horowitz, personal commun., 1990).

Because the concentration of Se in uraniferous shales is sometimes enriched considerably over that in most geochemical samples (Schultz and others, 1980) and additional Se reference samples are environmentally desirable, it is unfortunate that so few (3) laboratories contributed Se data for SDO–1. The range of those results, however, implies that SDO–1 contains less Se than many shales, approximately 5 μg/g in comparison to as much as 300 μg/g in the most enriched of the Cretaceous Pierre Shale samples (Schultz and others, 1980). All available Se data for SDO–1 was obtained by INAA; hydride analysis for Se could be subject to interferences similar to those that affected As analysis by that method.

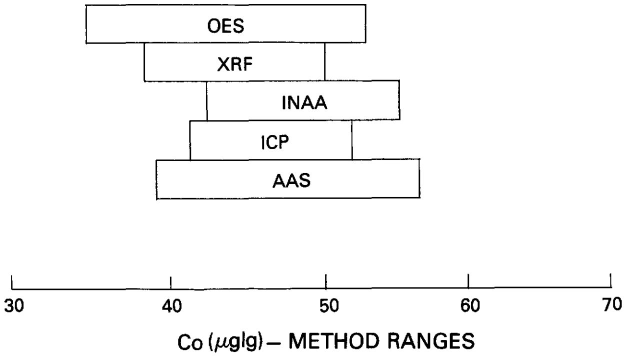

Figure 5. Co data ranges for each method of analysis.

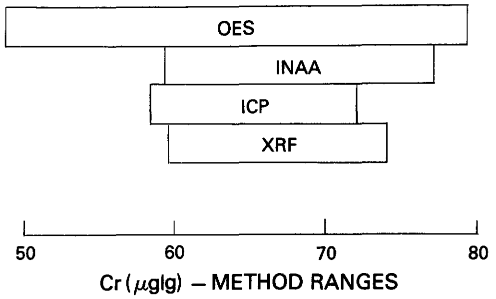

Figure 6. Cr data ranges for each method of analysis.

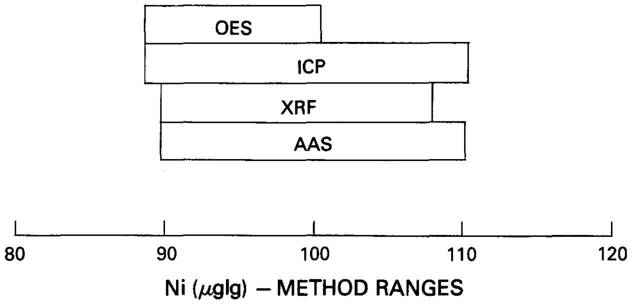

Figure 7. Ni data ranges for each method of analysis.

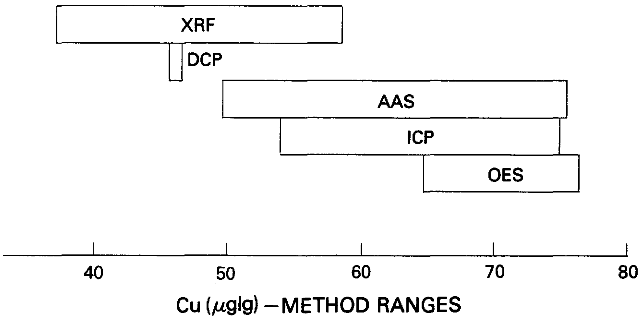

Figure 8. Cu data ranges for each method of analysis.

B was reported by relatively few laboratories, and only AES methods using DCP and dc arc excitation were used; thus, adequate confirmation of the interlaboratory averages by an independent technique was impossible. Therefore, despite the precision (rsd of 9 percent) of the intermethod result and an adequate number of laboratories (n=6) reporting B, the B value was not recommended.

Be was similarly determined only by atomic spectrometric techniques; for this element, results obtained by AAS, ICP–AES, and dc arc AES agreed. Confirmation by independent techniques is marginal; all methods are in the same general category, atomic spectrometry. The Be concentration is given as an average but not recommended, based on both an intermethod rsd of 17 percent and the lack of adequate independence of methods.

Co and Cr were determined by XRF, INAA, ICP–AES, and dc arc AES with very similar results regardless of method (figs. 5, 6). The same is true of Ni determined by XRF, ICP–AES, AAS, and dc arc AES (fig. 7). However, Cu determined by the same methods (fig. 8) shows a distinct difference between the XRF result and the three atomic spectroscopic results. In SDO–1, Cu could be associated with the pyritic fraction of the sample and therefore subject to sampling error within bottle as well as between bottle. This relation would make significant between-bottle variance, which could result in between-laboratory and between-method variance, very difficult to identify (Kane, 1992). We observe that the dc arc results are highest, whereas those for XRF, which uses the largest sample weight, are lowest. If sampling were the dominant source of discrepancy between methods, we would expect the reverse, based on sample-size considerations. The largest sample size should provide the highest result, and also the most accurate (Ingamells and Pitard, 1986); therefore, other factors must account for the intermethod discrepancy in Cu results. Possibly the XRF Cu result is biased due to a matrix effect such as that found by Kopp and Furman (chap. G, this vol.) for several major oxides.

Table 7 summarizes all of the trace element intermethod comparisons derived from the SDO–1 data base. The reader is referred to the table for conclusions on intermethod agreement for elements not already discussed.

We have already noted that the new methods being used for REE analyses, ICP–AES after separation and ICP–MS, are as accurate as the traditional INAA data for these elements. INAA is used by compilers of reference-sample data as the method of choice for a number of other analyses as well. The data in table 7, and the method-range data plotted in figures 3–8, do not support the superiority of INAA for many of those elements. For example, Co and Cr results (figs. 6, 7), discussed above, provide specific illustrations that XRF and ICP–AES both compare very favorably with INAA methods with respect to overall method accuracy and between-laboratory robustness. It is

Table 7. Between-method analysis of variance for trace elements whose concentrations are recommended

Element	Method means in µg/g							Probability method means the same
	XRF	ICP	NAA	AAS	OES dc arc	Sepn. ICP	DNA(U) or ICP–MS	
As		67.5±7.1	67.8±7.1	76.9±4.2				0.36
Ba	400±47.6	398±35.5	380	399	370±15			.825
Be		3.06±45		4.0	3.57±.62			.234
Ce	80.6±9.7	74.1±3.2	78.3±9.1		83.9±3.7			.64
Co	43.6±6.4	46.6±4.1	46.8±5.5	49.3±10.9	45.2±7.5			.85
Cr	68.2±5.9	65.8±4.6	68.4±8.1		60.5±11.2			.33
Dy			6.1±1.1			6.1±0.49	5.8	.94
Eu		1.7	1.7±0.03			1.7	1.5	
Ga	15.8±1.1	17.3			15.5±2.5			.62
La	35±5.5	37.6±2.4	38.3±4.5		39.4±4.2	35.9		.62
Li		32.0±2.5		28.8±5.4	32.4±15.3			.78
Mo	130.7	135.6±9.6	143.2±24.6		121.8±20.8			.47
Nb	13.8±3.5	10.3±5.7			9.5			.30
Nd	36.2	34.5±3.4	38.1±5.3			37.0±1.6	37.0	.78
Ni	98.1±9.4	106.4±8.2	91.8	98.9±13.9	95.1±5.8			.23
Pb		30.1±1.9		28.8±7.3	29.±5.7			.95
Sc		12.9±1.5	12.2±1.3		13.9±1.1			.29
Sm		8.2±1.7	8.8±2.3			7.93±0.48	6.80	.62
Sr	73.5±2.6	77.8±4.9			73.9±23.1			.76
Th		13.3±7.3	9.95±1.0					.24
U	55.0±2.2	42.8±2.2	46.0±5.96				55.6	.11
V	179.3±27.1	160.8±12	167	156.5	140.5±20.3			.13
Y	41±6.6	38.5±6.7	39.7	38.9±6.8		37.5		.88
Yb		3.11±0.24	3.61±0.36			3.15±0.31	3.40	.05
Zn	63.5±6.2	63.8±7.6	63.4±3.4	62.8±6.6	64.3±11.1			.99
Zr	166.7±13.1	156.2±13.6			173.8±48.3			.70
Number of elements determined by method	13	18	12	9	15	3	2	

more difficult to comment on comparability of within-laboratory precision for these methods. In general, where concentrations are high enough and counting times long enough, INAA can be more precise than the other methods, but these conditions are not always possible. Within-laboratory precision, however, is only one of several figures of merit in determining the general preferability of one analytical method over all others.

UPDATES OF THE ORIGINAL COMPILATION RECOMMENDED CONCENTRATIONS

Since the time SDO–1 recommended concentrations were first derived (March 1989) for inclusion in the July 1989 Special Issue of Geostandards Newsletter (Govindaraju, 1989), a number of new data contributions have been received and incorporated in the data base. Most of these appeared 1 year later in the full compilation (Kane and others, 1990); additions since then represent less than 1 percent of the total data base. The 1990 recommended concentrations for several rare earth elements differ from the 1989 concentrations (Govindaraju, 1989). Fluorine data received just prior to publication of this volume allowed the fluorine reported in table 1 of the Introduction to be upgraded from range to average. However, revision of most other initial recommended concentrations cannot be justified. It is important that reference-sample recommended concentrations be stable over time for them to be used for instrumental-calibration and method-validation purposes. Some change in a compilation iterated mean must occur any time new data is added to the data base. However, because the changes will have no statistical significance if the newly contributed data value lies within the uncertainty range of the initial recommended concentration, "updating" the recommended concentration based on that change is unwarranted. Several iterations of the compilation average for SiO_2, Al_2O_3, and several other constituents at different points during the characterization program illustrate changes that did not justify updating the original recommended concentration (table 8). Changes that did lead to updating of concentrations as initially reported for REE are shown in table 9. In these instances, intermethod agreement could be established for the updated data but not for the

Table 8. Samples for which newly added data do not lead to changes in recommended concentrations

Element/ oxide	Recommended based on data submitted before 3/89	New average 1/89	New average 2/91
Major in weight percent			
SiO_2	49.3±0.63 (26)	49.3±0.61 (27)	49.3±0.61 (29)
Al_2O_3	12.3±0.23 (22)	2.3±0.40 (27)	2.3±0.23 (28)
Fe_2O_3	9.34±0.21 (24)	.36±0.27 (30)	9.38±0.21 (34)
Trace in μg/g			
As	68.5±8.6 (7)	68.2±8.0 (8)	67.6±9.4 (11)
Ba	397±38 (17)	394±37 (19)	394±36 (20)
Ce	79.3±7.8 (18)	78.2±7.1 (23)	78.3±7.03 (24)
La	38.5±4.4 (18)	37.6±3.0 (29)	37.8±3.1 (30)
Mo	134±21 (15)	136±12 (17)	138±18 (19)
Zn	64.1±6.9 (23)	64.5±7.0 (25)	64.6±7.0 (26)

original (for example, Dy); or the required number of individual laboratory contributions increased enough to meet previously unmet criteria for recommending the concentration, that is, that a minimum of five laboratory results remain after all rejection cycles (for example, Eu).

CONCLUSION

This study indicates how much information is available in compilation data bases beyond the obvious recommended or average concentrations of individual constituents. Little of that information, however, is typically extracted or applied either to the derivation of recommended concentrations or to uses of the reference samples in calibration, quality control, or other applications. The statistical calculations themselves, having become almost totally automated with the availability of modern computers, are an essential starting point. However, improvement of reference-sample recommended concentrations and thoughtful use of those concentrations in all applications would benefit from a detailed examination of the wealth of information that these data bases provide. Perhaps this discussion will be a first step in that direction.

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Table 9. Examples for which newly added data result in changes in reported concentrations in μg/g except as noted

Element	Original Govindaraju, 1989		Update Kane and others, 1990		This volume	
Dy	5.7±0.99	Avg	6.0±0.65	Rec		
Er	2.5–4.7	Range	3.6±0.55	Avg		
Eu	1.6±0.22	Avg	1.6±0.22	Rec		
Gd	6.5±1.2	Avg	7.4±1.9	Avg		
Ho	1.1±3.3	Range	1.2±0.11	Avg		
Pr	6–13.8	Range	8.9±0.66	Rec		
Tm	0.34–0.56	Range	0.45±0.08	Avg		
F (%)	<0.010–<0.072	Range	<0.010–0.072	Range	0.0697±0.0089	AVG

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APPENDIX 1.
MAJOR/MINOR OXIDES: LABORATORY METHODS AND AVERAGES

SiO_2 data

Lab code/ method	Weight percent in sample
20–	23.00
30–	30.72
19–	48.10
3–ICP	48.29
2–XRF	48.43
57–XRF	48.50
6–XRF	48.57
4–RR	48.67
15–COLOR	48.73
17–RR	48.77
24–XRF	48.86
21–XRF	48.94
23–XRF	49.00
28–XRF	49.00
16–XRF	49.15
25–OES	49.22
13–XRF	49.24
58–ICP	49.28
14–CHEM	49.45
26–XRF	49.56
18–XRF	49.56
27–GRAV	49.90
36–ICP	49.90
37–	49.90
34–	49.90
31–	49.91
60–XRF	49.91
33–	49.95
5–XRF	50.05
1–RR	50.05
32–	50.06
29–COLOR	50.50
11–OES	54.53

Al_2O_3 data

Lab code/ method	Weight percent in sample
11–OES	11.34
24–XRF	11.65
12–NAA	11.68
20–	11.70
22–ICP	11.88
37–	12.00
23–XRF	12.00
33–	12.00
31–	12.04
60–XRF	12.04
15–COLOR	12.08
14–CHEM	12.08
17–RR	12.08
36–ICP	12.10
6–XRF	12.10
2–XRF	12.14
7–ICP	12.29
3–ICP	12.32
26–XRF	12.33
4–RR	12.34
50–ICP	12.38
19–	12.38
18–XRF	12.43
13–XRF	12.44
27–AAS	12.50
57–XRF	12.50
58–XRF	12.50
21–XRF	12.51
16–XRF	12.55
28–XRF	12.60
8–ICP	12.67
63–ICPMS	12.67
25–OES	12.68
29–AAS	12.70
5–XRF	13.02
34–	13.10
35–AA	13.10
1–RR	13.11
32–	14.01
30–NAA	17.45

$Fe_2O_3{}^*{}_{TOT}$ data	
Lab code/ method	Weight percent in sample
32–	0.28
30–NAA	2.31
20–	8.30
15–COLOR	8.30
31–	8.60
25–OES	8.82
22–ICP	9.01
19–	9.14
9–NAA	9.15
16–XRF	9.15
8–ICP	9.15
2–XRF	9.16
4–RR	9.17
13–XRF	9.19
37–	9.22
14–CHEM	9.22
1–RR	9.34
21–XRF	9.34
5–XRF	9.38
6–XRF	9.41
63–ICPMS	9.41
33–	9.43
60–NAA	9.43
10–NAA	9.44
50–ICP	9.45
55–NAA	9.45
17–RR	9.49
57–XRF	9.49
28–XRF	9.50
27–COLOR	9.54
7–ICP	9.54
11–OES	9.54
58–ICP	9.55
18–XRF	9.58
29–XRF	9.60
36–ICP	9.65
26–XRF	9.66
24–XRF	9.70
60–AAS	9.71
35–AAS	9.75
34–	9.76
12–NAA	10.12
56–NAA	10.19

* For reporting of total iron only; does not accurately represent iron speciation in sample.

FeO data	
Lab code/ method	Weight percent in sample
24–CHEM	1.31
3–CHEM	2.25
19–CHEM	2.94
14–CHEM	5.63

Fe_2O_3 data	
Lab code/ method	Weight percent in sample
14–CHEM	3.03
3–CHEM	7.17
24–CHEM	8.26

CaO data	
Lab code/ method	Weight percent in sample
36–ICP	0.11
30–NAA	.13
11–OES	.84
33–	.89
23–XRF	.90
8–ICP	.96
24–XRF	.97
25–OES	.97
12–NAA	1.01
31–	1.01
37–	1.01
60–XRF	1.01
21–XRF	1.03
50–ICP	1.04
2–XRF	1.05
29–AAS	1.05
16–XRF	1.05
13–XRF	1.05
58–ICP	1.06
14–CHEM	1.06
19–	1.06
32–	1.06
26–XRF	1.06
18–XRF	1.06
1–RR	1.06
6–XRF	1.07
15–AAS	1.08
7–ICP	1.08
5–XRF	1.09
28–XRF	1.10
57–XRF	1.10
17–RR	1.11
22–ICP	1.12
27–CHEM	1.12
4–RR	1.13
34–	1.20
35–AAS	1.20
3–ICP	1.37
20–	1.60

MgO data	
Lab code/ method	Weight percent in sample
37–	1.29
31–	1.29
60–XRF	1.29
26–XRF	1.43
12–NAA	1.45
36–ICP	1.47
14–AAS	1.48
25–OES	1.49
58–ICP	1.49
33–	1.51
29–AAS	1.51
13–XRF	1.52
19–	1.52
8–ICP	1.52
17–RR	1.53
21–XRF	1.53
28–AAS	1.53
6–XRF	1.54
7–ICP	1.54
5–XRF	1.54
2–XRF	1.55
1–RR	1.55
4–RR	1.57
50–ICP	1.57
15–AAS	1.57
18–XRF	1.59
35–AAS	1.59
24–XRF	1.59
34–	1.59
27–CHEM	1.59
20–	1.60
57–XRF	1.60
11–OES	1.63
16–XRF	1.65
22–ICP	1.66
3–ICP	1.74
32–	1.81

Na_2O data	
Lab code/ method	Weight percent in sample
26–XRF	0.25
24–XRF	.26
22–ICP	.29
4–RR	.33
13–XRF	.34
25–OES	.35
6–XRF	.35
32–	.36
10–NAA	.36
15–FP	.37
57–XRF	.37
2–XRF	.37
17–RR	.37
58–AAS	.38
9–NAA	.38
12–NAA	.38
8–ICP	.38
7–ICP	.38
16–XRF	.38
29–AAS	.38
31–	.38
37–	.38
18–XRF	.39
55–NAA	.39
50–ICP	.39
26–XRF	.39
1–RR	.40
5–FP	.42
27–AAS	.42
36–ICP	.42
56–NAA	.42
14–AAS	.43
19–	.44
11–OES	.44
21–XRF	.51
20–	.60
35–AAS	.60
34–	.60
23–XRF	.67
3–ICP	.95

K_2O data	
Lab code/ method	Weight percent in sample
30–NAA	2.68
22–ICP	2.79
25–OES	2.80
15–FM	2.95
23–XRF	3.00
31–	3.06
60–XRF	3.06
4–RR	3.16
13–XRF	3.18
19–	3.20
14–CHEM	3.23
2–XRF	3.24
12–NAA	3.27
37–	3.29
16–XRF	3.29
6–XRF	3.29
28–XRF	3.30
21–XRF	3.31
50–ICP	3.34
26–XRF	3.35
55–NAA	3.35
17–RR	3.36
36–ICP	3.36
33–	3.37
27–AAS	3.37
7–ICP	3.37
18–XRF	3.37
1–RR	3.39
5–FP	3.40
35–AAS	3.41
34–	3.41
24–XRF	3.43
55–NAA	3.44
60–NAA	3.45
32–	3.46
31–	3.51
3–ICP	3.60
20–	3.70
11–OES	3.82
8–ICP	4.60

TiO_2 data	
Lab code/ method	Weight percent in sample
30–NAA	0.34
7–ICP	.48
50–ICP	.48
3–ICP	.51
29–COLOR	.60
23–XRF	.60
12–NAA	.62
11–OES	.63
25–OES	.63
17–RR	.67
2–XRF	.68
20–	.68
19–	.68
13–XRF	.68
36–ICP	.69
24–XRF	.69
28–XRF	.69
4–RR	.70
22–ICP	.70
6–XRF	.70
32–	.70
21–XRF	.70
16–XRF	.70
15–OES	.70
15–COLOR	.72
14–CHEM	.72
8–ICP	.73
1–RR	.73
58–ICP	.74
18–XRF	.74
27–COLOR	.74
37–	.74
57–XRF	.74
60–XRF	.74
5–XRF	.75
31–	.75
26–XRF	.78
35–AAS	1.01

P_2O_5 data	
Lab code/ method	Weight percent in sample
18–XRF	0.07
3–ICP	.07
19–	.08
21–XRF	.09
20–	.10
34–	.10
28–COLOR	.10
35–AAS	.10
37–	.10
60–XRF	.10
14–CHEM	.10
5–COLOR	.11
15–COLOR	.11
27–COLOR	.11
13–XRF	.11
22–ICP	.11
33–	.11
2–XRF	.11
24–XRF	.11
36–ICP	.11
16–XRF	.11
58–COLOR	.11
7–ICP	.12
29–COLOR	.12
6–XRF	.12
4–RR	.12
26–XRF	.12
57–XRF	.12
8–ICP	.13
1–RR	.14
50–ICP	.14
17–RR	.15
25–OES	.24
11–OES	.29

MnO data	
Lab code/ method	Weight percent in sample
6–XRF	0.030
25–OES	.030
26–XRF	.031
3–ICP	.032
1–RR	.038
7–ICP	.039
25–AAS	.039
13–XRF	.039
11–OES	.039
58–ICP	.039
18–XRF	.039
15–OES	.040
36–ICP	.040
4–RR	.040
17–RR	.040
21–XRF	.040
37–	.040
28–XRF	.040
14–AAS	.041
36–ICP	.041
50–ICP	.041
35–AAS	.042
29–AAS	.042
12–NAA	.043
37–	.043
27–AAS	.043
8–ICP	.046
22–ICP	.046
19–	.050
2–XRF	.050
24–XRF	.080

LOI data	
Lab code/ method	Weight percent in sample
3–GRAV	19.56
1–GRAV	19.56
27–GRAV	19.78
13–GRAV	20.83
18–GRAV	20.91
58–GRAV	21.37
16–GRAV	21.38
6–GRAV	21.57
4–GRAV	21.63
17–GRAV	21.82
21–GRAV	21.90
15–GRAV	21.93
57–GRAV	22.00
26–GRAV	22.35
19–GRAV	22.37
2–GRAV	22.84
22–GRAV	23.08
20–GRAV	33.00

C_{TOT} data	
Lab code/ method	Weight percent in sample
20–	8.97
27–	9.27
7–	9.85
6–	9.96
19–	9.96
13–	9.96
8–	9.98
28–	10.00
14–	10.26
23–	10.36
29–	10.40
30–	10.40
34–	10.40
32–	10.43
60–COMB	10.53
38–	10.89
39–	11.80
31–	13.79

Hydrogen (percent)	
Lab code/ rejection method	Weight percent in sample
39–	1.24
30–	1.30
38–	1.30
23–	1.33
32–	1.34
This work	1.34
34–	1.35
29–	1.40
55–	1.45
31–	1.83

Nitrogen (percent)	
Lab code/ rejection method	Weight percent in sample
31–	0.31
38–	.31
34–	.32
This work	.33
32–	.34
23–	.40
30–	.40
39–	1.21

Constitutional water (percent)	
Lab code/ rejection method	Weight percent in sample
Compilation average	2.93
17–	4.41
14–	7.12

APPENDIX 2.
TRACE ELEMENTS: LABORATORY METHODS AND AVERAGES

Ag data

Lab code/ method	µg/g in sample
15–AAS	0.0944
15–OES	.1650
58–AAS	<.40
27–OES	<.40
3–ICP	<.50
57–DCP	<.50
7–ICP	<2
11–OES	<2
42–OES	<3
12–NAA	<4

As data

Lab code/ method	µg/g in sample
3–ICP	<10.0
7–HYD	38
14–XRF	50.3
21–XRF	55.0
7–ICP	62.5
10–NAA	62.7
50–ICP	66.1
57–FAA	69.0
8–ICP	72.5
12–NAA	72.8
29–HGA	74.0
60–NAA	79
55–NAA	79.0
46–HGA	79.8
58–AAS	100
23–HGA	104

Au data

Lab code/ method	µg/g in sample
15–AAS	0.0014
23–NAA	.0020
13–XRF	.0035
12–NAA	<.010
58–AAS	<.10
57–DCP	<2
7–ICP	<8

B data

Lab code/ method	µg/g in sample
3–ICP	92.5
15–OES	120
27–OES	120
60–OESa	120
16–OES	129
11–OES	130
57–DCP	130
60–OESc	140
42–OES	145
40–OES	170

Ba data

Lab code/ method	µg/g in sample
3–ICP	211
21–XRF	318
22–ICP	335
40–OES	360
11–OES	363
2–XRF	369
12–NAA	380
17–ICP	381
13–XRF	385
43–XRF	388
15–OES	390
15–AAS	398
41–XRF	403
10–NAA	403
7–ICP	407
8–ICP	415
27–ICP	420
44–XRF	424
26–ICP	431
15–XRF	444
24–XRF	473
57–XRF	481
58–ICP	495
42–OES	529
55–NAA	550
10–NAA	598
27–OES	600
9–NAA	633
15–OES	640
25–OES	743

Be data	
Lab code/ method	µg/g in sample
58–ICP	2.00
8–ICP	2.75
22–ICP	2.78
17–ICP	2.93
7–ICP	3.00
15–OES	3.01
50–ICP	3.09
16–OES	3.48
26–ICP	3.85
2–AAS	4.0
11–OES	4.25
57–DCP	5.00
40–OES	5.83

Bi data	
Lab code/ method	µg/g in sample
57–DCP	0.2
2–XRF	<2
3–ICP	<10
7–ICP	<10
21–XRF	<30

Br data	
Lab code/ method	µg/g in sample
12–NAA	5
60–NAA	3.6

Cd data	
Lab code/ method	µg/g in sample
57–DCP	<0.2
29–HGA	<.5
58–ICP	1
7–ICP	<2
11–OES	<3
27–ICP	7
21–XRF	<20

Ce data	
Lab code/ method	µg/g in sample
3–ICP	63.0
7–NAA	64.0
14–EXTR/ICP	65.0
26–ICP	68.0
50–ICP	68.7
2–XRF	70.0
7–ICP	70.5
9–NAA	70.8
14–SEPN/ICP	71.3
41–XRF	71.8
49–SEPN/ICP	71.8
43–XRF	72.3
57–ICPMS	73.2
56–NAA	73.7
8–NAA	74.2
8–ICP	75.0
24–SEPN/ICP	76.2
63–ICPMS	76.2
17–SEPN/ICP	76.7
7–SEPN/ICP	76.8
60–NAA	77.4
44–XRF	78.5
10–NAA	78.5
40–OES	80.2
11–OES	84.0
5–NAA	85.0
15–NAA	87.3
16–OES	87.5
13–XRF	89.7
21–XRF	90.0
24–XRF	92.0
12–NAA	100

Cl data	
Lab code/ method	µg/g in sample
60–XRF	90
55–NAA	94
12–NAA	116

Co data	
Lab code/ method	µg/g in sample
60–OESc	35
40–OES	36.5
25–OES	37.5
2–XRF	39.8
5–AAS	40.0
21–XRF	40.0
11–OES	40.3
22–ICP	41.8
25–AAS	42.0
17–ICP	42.5
5–NAA	43.1
9–NAA	43.5
60–NAA	44
26–ICP	44.0
10–NAA	44.4
58–ICP	44.5
45–AAS	46.5
12–NAA	46.8
3–ICP	47.0
8–ICP	48.0
56–NAA	48.9
60–OESa	49
27–OES	50.0
24–XRF	51.0
7–ICP	51.3
50–ICP	51.4
57–ICP	52.0
27–ICP	52.0
42–OES	53.0
15–OES	53.0
15–NAA	56.3
23–AAS	57.0

Cr data	
Lab code/ method	µg/g in sample
42–OES	47.8
60–OESc	50
25–OES	51.5
11–OES	55.8
60–OESa	56
40–OES	56.2
57–DCP	58.0
3–ICP	59.0
9–NAA	59.6
14–XRF	60.3
26–ICP	61.0
55–NAA	61.0
60–NAA	61
13–XRF	64.3
10–NAA	64.5
58–ICP	65.0
8–ICP	65.0
41–XRF	66.3
50–ICP	66.3
27–ICP	67.0
22–ICP	67.0
21–XRF	68.4
56–NAA	69.3
17–ICP	70.0
23–OES	70.0
12–NAA	71.6
7–ICP	71.8
15–ICP	73.0
44–XRF	74.8
2–XRF	75.3
29–HGA	77.0
15–NAA	78.0
27–OES	80.0
43–XRF	95.8
24–XRF	103

Cs data

Lab code/ method	µg/g in sample
57–NAA	5.00
5–NAA	5.23
9–NAA	5.97
10–NAA	6.42
56–NAA	6.97
60–NAA	7
12–NAA	7.32
2–XRF	7.75
15–NAA	8.65
5–FLPHO	11.5

Cu data

Lab code/ method	µg/g in sample
4–XRF	29.0
21–XRF	37.0
57–DCP	46.0
2–XRF	47.5
28–XRF	50.0
45–AAS	50.3
14–XRF	51.8
58–ICP	53.5
43–XRF	54.3
5–AAS	54.5
60–OESc	55
7–ICP	56.8
26–ICP	58.0
41–XRF	58.3
8–ICP	58.3
50–ICP	58.7
44–XRF	59.3
15–OES	60.0
27–OES	60.0
15–AAS	61.0
22–ICP	61.3
3–ICP	62.0
60–AAS	63
11–OES	64.8
29–HGA	67.0
16–OES	69.5
60–OESa	73
23–AAS	74.0
17–ICP	74.5
27–AAS	75.0
40–OES	75.5
42–OES	225

Dy data

Lab code/ method	µg/g in sample
3–ICP	4.75
8–SEPN/ICP	5.20
57–ICPMS	5.80
63–ICPMS	5.90
26–SEPN/ICP	6.00
24–SEPN/ICP	6.07
49–SEPN/ICP	6.10
14–SEPN/ICP	6.25
12–NAA	6.50
17–SEPN/ICP	6.72
7–NAA	6.90
60–NAA	7.1
14–EXTR/ICP	7.11
7–SEPN/ICP	7.30

Er data

Lab code/ method	µg/g in sample
8–SEPN/ICP	2.90
7–SEPN/ICP	3.10
49–SEPN/ICP	3.26
26–SEPN/ICP	3.40
57–ICPMS	3.40
17–SEPN/ICP	3.55
14–SEPN/ICP	3.81
14–SEPN/ICP	3.98
3–ICP	4.75

Eu data

Lab code/ method	µg/g in sample
3–ICP	<1
9–NAA	1.43
5–NAA	1.46
10–NAA	1.47
14–SEPN/ICP	1.47
7–NAA	1.50
12–NAA	1.63
49–SEPN/ICP	1.65
14–EXTR/ICP	1.67
24–SEPN/ICP	1.68
50–ICP	1.68
63–ICPMS	1.68
26–SEPN/ICP	1.70
57–ICPMS	1.71
8–SEPN/ICP	1.72
56–NAA	1.77
60–NAA	1.9
17–SEPN/ICP	1.95
7–ICP	<2
7–SEPN/ICP	2.0
15–NAA	2.05

F data

Lab code/ method	μg/g in sample
14–	<100
60–ISE	534
55–ISE	590
24–PIGE	687
18–	720
4–ISE	727
61–IC	742
61–IC	780
62–IC	808

Ga data

Lab code/ method	μg/g in sample
3–ICP	<10
15–OES	14.0
21–XRF	15.0
11–OES	16.0
2–XRF	16.5
50–ICP	16.7
25–OES	16.8
7–ICP	17.3
8–ICP	17.3
40–OES	18.5
55–NAA	19.0
60–NAA	19
58–ICP	<20.0
23–OES	20.0
12–NAA	23.6
57–ICP	24.0
5–AAS	27.5

Gd data

Lab code/ method	μg/g in sample
3–ICP	5.0
26–SEPN/ICP	5.1
7–NAA	6.2
8–NAA	6.9
57–ICPMS	6.9
14–SEPN/ICP	7.1
17–SEPN/ICP	7.3
24–SEPN/ICP	7.8
49–SEPN/ICP	7.8
63–ICPMS	7.8
14–EXTR/ICP	8.1
7–SEPN/ICP	9.1
8–SEPN/ICP	9.7
40–OES	11.5

Hf data

Lab code/ method	μg/g in sample
9–NAA	3.28
5–NAA	3.90
57–NAA	4.00
9–NAA	4.03
10–NAA	4.38
2–XRF	4.50
60–NAA	4.6
56–NAA	4.62
12–NAA	5.80

Hg data

Lab code/ method	μg/g in sample
27–OES	<0.05
57–CHEM	.088
48–CVAA	.096
3–ICP	.18
23–CVAA	.19
47–CVAA	.29
12–NAA	1.3
29–CVAA	3.0

Ho data

Lab code/ method	μg/g in sample
3–ICP	<1
8–SEPN/ICP	1.07
57–ICPMS	1.08
49–SEPN/ICP	1.14
14–SEPN/ICP	1.19
7–SEPN/ICP	1.2
26–SEPN/ICP	1.3
14–EXTR/ICP	1.38
7–ICP	<4

La data	
Lab code/ method	µg/g in sample
44–XRF	26.7
50–ICP	33.1
10–NAA	33.3
9–NAA	33.7
2–XRF	33.8
14–SEPN/I	35.0
49–SEPN/I	35.2
41–XRF	35.5
57–ICPMS	35.5
3–ICP	35.5
24–XRF	35.9
63–ICPMS	35.9
7–NAA	36.0
40–OES	36.2
58–ICP	37.0
15–OES	37.0
7–SEPN/IC	37.4
43–XRF	37.5
17–ICP	37.8
8–SEPN/IC	37.9
26–ICP	38.0
14–EXTR/I	38.5
7–ICP	38.8
56–NAA	39.1
16–OES	39.5
12–NAA	40.2
8–ICP	41.0
15–NAA	41.5
13–XRF	41.7
5–NAA	42.8
60–NAA	42.8
11–OES	45.3
23–OES	50.0
27–OES	<60
21–XRF	70.0

Li data	
Lab code/ method	µg/g in sample
15–OES	21.62
5–AAS	22.5
27–ICP	28.0
22–ICP	31.2
60–AAS	31.8
57–AAS	32.0
50–ICP	32.7
7–ICP	33.7
8–ICP	34.2
11–OES	43.2

Lu data	
Lab code/ method	µg/g in sample
57–ICPMS	0.42
26–SEPN/ICP	.43
7–SEPN/ICP	.43
49–SEPN/ICP	.44
8–SEPN/ICP	.45
24–SEPN/ICP	.45
63–ICPMS	.45
17–SEPN/ICP	.47
10–NAA	.48
14–SEPN/ICP	.49
9–NAA	.50
7–NAA	.53
60–NAA	.54
14–EXTR/ICP	.55
15–NAA	.63
56–NAA	.68
12–NAA	.69
5–NAA	.96
3–ICP	4.0

Mo data	
Lab code/ method	µg/g in sample
50–ICP	108
40–OES	109
27–OES	120
23–COLOR	122
7–ICP	122
10–NAA	126
2–XRF	131
27–ICP	132
16–OES	133
3–ICP	134
15–OES	140
22–ICP	142
8–ICP	148
11–OES	150
58–ICP	150
55–NAA	155
60–NAA	157
60–OESc	160
12–NAA	161
29–COLOR	181
60–OESa	190
28–XRF	193
14–XRF	198
44–XRF	215

Nb data	
Lab code/ method	µg/g in sample
50–ICP	5.3
8–ICP	6.0
7–ICP	6.3
40–OES	9.5
24–XRF	10.0
14–XRF	10.8
17–ICP	12.0
2–XRF	12.0
41–XRF	12.3
22–ICP	12.3
13–XRF	12.3
18–XRF	12.5
57–XRF	17.0
44–XRF	17.1
58–ICP	20.0
43–XRF	20.3
11–OES	<25

Nd data	
Lab code/ method	µg/g in sample
3–ICP	30.8
10–NAA	32.2
5–NAA	33.0
7–NAA	35.0
14–SEPN/I	35.6
50–ICP	35.7
14–EXTR/I	35.7
17–SEPN/I	36.2
2–XRF	36.2
49–SEPN/I	36.3
57–ICPMS	37.0
7–ICP	37.2
56–NAA	37.4
63–ICPMS	38.2
24–SEPN/ICP	38.3
8–SEPN/IC	38.6
15–NAA	38.8
9–NAA	39.3
7–SEPN/IC	39.4
16–OES	40.0
12–NAA	40.4

Ni data	
Lab code/ method	µg/g in sample
13–XRF	84.0
5–AAS	86.3
25–AAS	88.5
40–OES	89.3
58–ICP	89.5
25–OES	89.9
11–OES	90.0
28–XRF	90.0
45–AAS	90.3
10–NAA	91.8
2–XRF	93.3
26–ICP	94.0
44–XRF	94.9
55–NAA	98
17–ICP	99.3
42–OES	99.8
57–DCP	100
27–OES	100
15–OES	101
41–XRF	102
14–XRF	106
43–XRF	108
27–ICP	109
8–ICP	110
7–ICP	110
29–HGA	111
3–ICP	116
15–AAS	117
22–ICP	128
23–AAS	128

Pb data

Lab code/ method	µg/g in sample
27–OES	10.0
11–OES	17.5
23–OES	20.0
14–XRF	20.5
5–AAS	21.0
57–DCP	24.0
50–ICP	25.2
15–OES	26.0
7–ICP	28.0
25–AAS	28.5
16–OES	29.5
15–AAS	30.0
3–ICP	30.5
2–XRF	30.8
8–ICP	31.8
60–AAS	33
40–OES	34.5
45–AAS	35.5
60–OESc	37
60–OESa	38
28–AAS	40.0
42–OES	42.5

Pr data

Lab code/ method	µg/g in sample
14–SEPN/ICP	8.0
2–XRF	8.0
14–EXTR/ICP	8.7
57–ICPMS	8.7
49–SEPN/ICP	9.2
26–SEPN/ICP	9.4
8–SEPN/ICP	9.5
7–SEPN/ICP	9.7
3–ICP	13.8

Rb data

Lab code/ method	µg/g in sample
58–XRF	114
25–OES	117
2–XRF	117
5–NAA	121
44–XRF	122
14–XRF	124
24–XRF	124
41–XRF	124
10–XRF	125
17–ICP	125
18–XRF	126
55–NAA	127
60–NAA	127
10–NAA	128
13–XRF	132
43–XRF	134
15–NAA	149
12–NAA	154

Sb data

Lab code/ method	µg/g in sample
57–AAS	2.3
9–NAA	4.12
10–NAA	4.60
12–NAA	4.77
3–NAA	<10

Sc data	
Lab code/ method	µg/g in sample
5–NAA	10.3
50–ICP	11.8
3–ICP	11.8
22–ICP	12.0
7–ICP	12.0
57–ICP	12.0
9–NAA	12.3
40–OES	12.6
10–NAA	12.7
11–OES	12.8
14–SEPN/ICP	12.8
58–XRF	14.0
56–NAA	14.0
2–XRF	14.3
17–ICP	14.3
15–OES	14.4
23–OES	15.0
55–NAA	15.2
8–ICP	15.3
15–NAA	18.3

Se data	
Lab code/ method	µg/g in sample
60–NAA	1.9
59–INAA	2.68
12–NAA	3
10–NAA	6.8

Sm data	
Lab code/ method	µg/g in sample
12–NAA	6.4
57–ICPMS	6.8
56–NAA	7.41
3–ICP	7
26–SEPN/ICP	7.5
8–NAA	7.5
14–SEPN/ICP	7.5
49–SEPN/ICP	7.6
24–SEPN/ICP	7.6
63–ICPMS	7.6
10–NAA	7.7
8–SEPN/ICP	8.2
9–NAA	8.3
17–SEPN/ICP	8.4
15–NAA	8.6
14–EXTR/ICP	8.7
60–NAA	8.7
7–ICP	9.4
5–NAA	13

Sn data	
Lab code/ method	µg/g in sample
27–OES	2.5
44–XRF	2.7
15–OES	3.2
57–XRF	5.0
2–XRF	3.3
16–OES	5.3
14–XRF	<7
11–OES	<10
3–ICP	<10
7–ICP	<10

Sr data

Lab code/ method	µg/g in sample
25–OES	31.5
42–OES	41.5
3–ICP	68.0
44–XRF	68.3
27–OES	70.0
11–OES	72.0
14–XRF	72.0
13–XRF	72.7
57–XRF	73.0
21–XRF	73.0
2–XRF	73.8
18–XRF	74.5
8–XRF	75.8
24–XRF	76.0
41–XRF	76.0
43–XRF	76.0
22–ICP	77.5
50–ICP	78.3
17–ICP	78.8
15–OES	80.0
27–ICP	80.0
8–ICP	80.3
26–ICP	83.5
55–NAA	93.0
40–OES	106.0
16–OES	128
23–OES	150

Ta data

Lab code/ method	µg/g in sample
60–NAA	1.1
9–NAA	1.03
10–NAA	1.07
5–NAA	1.08
56–NAA	1.08
12–NAA	1.19
15–NAA	1.36
2–XRF	<3
2–XRF	4
3–ICP	<10
7–ICP	<40

Tb data

Lab code/ method	µg/g in sample
57–ICPMS	0.80
14–SEPN/ICP	.93
14–EXTR/ICP	.96
26–SEPN/ICP	1.00
7–SEPN/ICP	1.00
8–SEPN/ICP	1.00
60–NAA	1.2
7–NAA	1.10
10–NAA	1.15
9–NAA	1.16
15–NAA	1.26
56–NAA	1.28
49–SEPN/ICP	1.40
5–NAA	1.46
12–NAA	1.65
3–ICP	3.25

Th data

Lab code/ method	µg/g in sample
57–NAA	8.10
50–ICP	9.20
55–NAA	9.5
60–NAA	9.5
10–ICP	9.77
9–NAA	9.82
56–NAA	9.95
17–ICP	10.35
5–NAA	10.60
12–NAA	10.62
7–ICP	11.00
15–NAA	11.21
3–ICP	26.25

Tm data

Lab code/ method	µg/g in sample
57–ICPMS	0.30
27–OES	.34
8–SEPN/ICP	.34
49–SEPN/ICP	.44
26–SEPN/ICP	.46
14–SEPN/ICP	.49
7–SEPN/ICP	.5
7–NAA	.55
9–NAA	.56

U data

Lab code/ method	µg/g in sample
57–NAA	34.2
3–ICP	40.5
10–NAA	40.8
17–ICP	43.2
50–ICP	44.8
12–NAA	46.2
56–NAA	46.6
14–XRF	48.5
9–NAA	50.7
29–NAA	51.0
15–NAA	51.8
55–NAA	52
60–NAA	52
28–NAA	54.0
23–DNA	55.6
2–XRF	61.5

V data

Lab code/ method	µg/g in sample
25–OES	88
42–OES	123
40–OES	133
3–ICP	139
15–AAS	145
8–ICP	158
11–OES	158
13–XRF	158
17–ICP	159
57–DCP	160
58–ICP	160
23–OES	161
50–ICP	164
26–ICP	165
27–ICP	166
12–NAA	167
21–XRF	168
29–COLOR	168
15–OES	170
27–OES	170
2–XRF	172
7–ICP	179
22–ICP	179
24–XRF	219
28–AAS	266

W data

Lab code/ method	µg/g in sample
16–OES	<0.8
2–XRF	<3
57–NAA	<3
12–NAA	3.34
58–ICP	5
27–OES	<60

Y data

Lab code/ method	µg/g in sample
3–ICP	29.0
57–ICP	30.0
8–SEPN/ICP	31.0
40–OES	31.2
49–ICP	31.2
44–XRF	32.4
41–XRF	32.5
7–ICP	34.0
14–SEPN/ICP	34.9
26–ICP	35.0
24–XRF	35.0
50–ICP	35.6
58–ICP	36.5
18–XRF	37.5
7–NAA	39.7
13–XRF	40.0
14–EXTR/ICP	40.4
8–ICP	41.5
11–OES	41.8
21–XRF	42.0
43–XRF	42.3
17–ICP	42.8
16–OES	43.8
22–ICP	45.3
14–XRF	45.5
17–SEPN/ICP	49.5
2–XRF	49.8
23–OES	50.0
15–OES	50.0

Yb data	
Lab code/ method	µg/g in sample
26–SEPN/ICP	2.80
55–NAA	2.9
60–NAA	2.9
7–ICP	3.00
3–ICP	3.00
23–ICP	3.00
50–ICP	3.01
24–SEPN/ICP	3.04
63–ICPMS	3.04
14–SEPN/ICP	3.08
7–SEPN/ICP	3.10
49–SEPN/ICP	3.11
8–SEPN/ICP	3.15
9–NAA	3.33
10–NAA	3.39
7–NAA	3.40
57–ICPMS	3.40
56–NAA	3.52
17–ICP	3.55
14–EXTR/ICP	3.80
12–NAA	3.92
15–NAA	4.30
15–OES	5.00
40–OES	5.05
16–OES	5.23

Zn data	
Lab code/ method	µg/g in sample
12–NAA	<30
15–OES	50.0
17–ICP	55.5
5–AAS	55.8
14–XRF	56.5
21–XRF	57.0
7–ICP	57.5
45–AAS	59.3
50–ICP	59.4
28–AAS	60.0
43–XRF	60.3
10–NAA	61.0
8–ICP	62.5
24–XRF	64.0
41–XRF	64.3
40–OES	65.0
9–NAA	65.8
29–HGA	67.0
58–ICP	68.0
57–DCP	70.0
25–AAS	70.5
44–XRF	71.3
22–ICP	71.5
2–XRF	71.8
3–ICP	72.0
27–AAS	72.0
15–OES	73.0
23–	76.0
27–OES	100

Zr data	
Lab code/ method	µg/g in sample
3–ICP	101
40–OES	112
60–OESa	130
22–ICP	141
23–OES	150
41–XRF	153
2–XRF	156
17–ICP	159
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Chapter B

Determination of Major and 11 Trace Elements (XRF), Gold (AAS), Carbon and Sulfur (COUL) in USGS Devonian Ohio Shale SDO–1

By OTMAR SPIES, BERNHARD STRIBRNY, JOSEF KONOPASEK, and HANS URBAN

U.S. GEOLOGICAL SURVEY BULLETIN 2046

THE USGS REFERENCE SAMPLE DEVONIAN OHIO SHALE SDO–1

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Determination of Major and 11 Trace Elements (XRF), Gold (AAS), Carbon and Sulfur (COUL) in USGS Devonian Ohio Shale SDO–1

By Otmar Spies, Bernhard Stribrny, Josef Konopasek, *and* Hans Urban[1]

Abstract

An X-ray fluorescence (XRF) analytical program for the determination of 10 major and 11 trace elements in rock samples has been developed using a glass bead 32 mm in diameter. The method was applied to the characterization of the shale SDO–1 as a reference sample in conjunction with the Metalliferous Black Shales Project of the International Geologic Congress. Additionally, loss on ignition and carbon and sulfur, using coulometry (COUL), were determined as major constituents in SDO–1; and trace gold was determined by graphite furnace atomic absorption spectrometry (AAS) after fire assay preconcentration. The data were used in establishing recommended concentrations for constituents in the reference sample.

INTRODUCTION

As a contribution to the International Geologic Congress Project (IGCP) 254, “Metalliferous Black Shales,” our working group investigated black-shale-hosted copper, gold, and lead-zinc deposits in the Northeastern Rhenish Massif of central Germany (Stribrny, 1987; Stribrny and others, 1988). These deposits occur in the Lower Carboniferous Variscan folded black shale series composed of black shales, black lydites, siliceous limestones, and clay shales. Commonly, these rocks host low-grade concentrations of stratabound sulfides, which are interpreted as sedimentary-exhalative depositions. Intraformational mobilizations and migrations of metals and their reprecipitation in physico-chemical traps led locally to minable ores. Additional metal concentrations were related to supergene processes (Stribrny and Urban, 1989).

EXPERIMENT PARAMETERS

Determination of Major and Trace Elements by X-ray Fluorescence Analysis

An X-ray fluorescence (XRF) analytical program (called GEO, fig. 1) for the determination of 10 major and 11 trace elements in rock samples has been developed using a glass bead 32 mm in diameter. Fusions of rock samples were made using a flux-to-sample ratio of 4:1. Calibration was established with 41 international geochemical reference standards.

Sample Preparation

For the sample preparation, a fusion method has been adopted. First, the rock powders were dried at 105°C for 3 hours, and the flux (Merck A12 Spectromelt=66 percent $Li_2B_4O_7$+34-percent $LiBO_2$) was heated at 450°C for 3 hours. Samples containing nonoxides as sulfides and organic carbon required further pretreatment prior to the fusion. For this pretreatment, 1.5 g NH_4NO_3 was added to the mixture of 1 g rock powder and 4 g Spectromelt. Heating the Pt-Au crucible at 450°C for 1 hour disassociated the NH_4NO_3 with subsequent oxidation of nonoxides. After oxidation, 20 mg NH_4Br was added before proceeding with the fusions to avoid adhesion and erosion of the nonwetting Pt-Au alloy crucible.

The samples were then mixed with flux at a 4:1 flux-to-sample ratio by weight. The mixtures were fused at 1,200°C for 6 minutes in the Pt-Au crucible utilizing a RF induction heater with mechanical agitation (type: Kontron-Rotomelt). At the end of fusion the crucible was inverted, and the melt was cast into a polished mold held at 500°C. The mold was then removed from the hot plate and cooled to room temperature.

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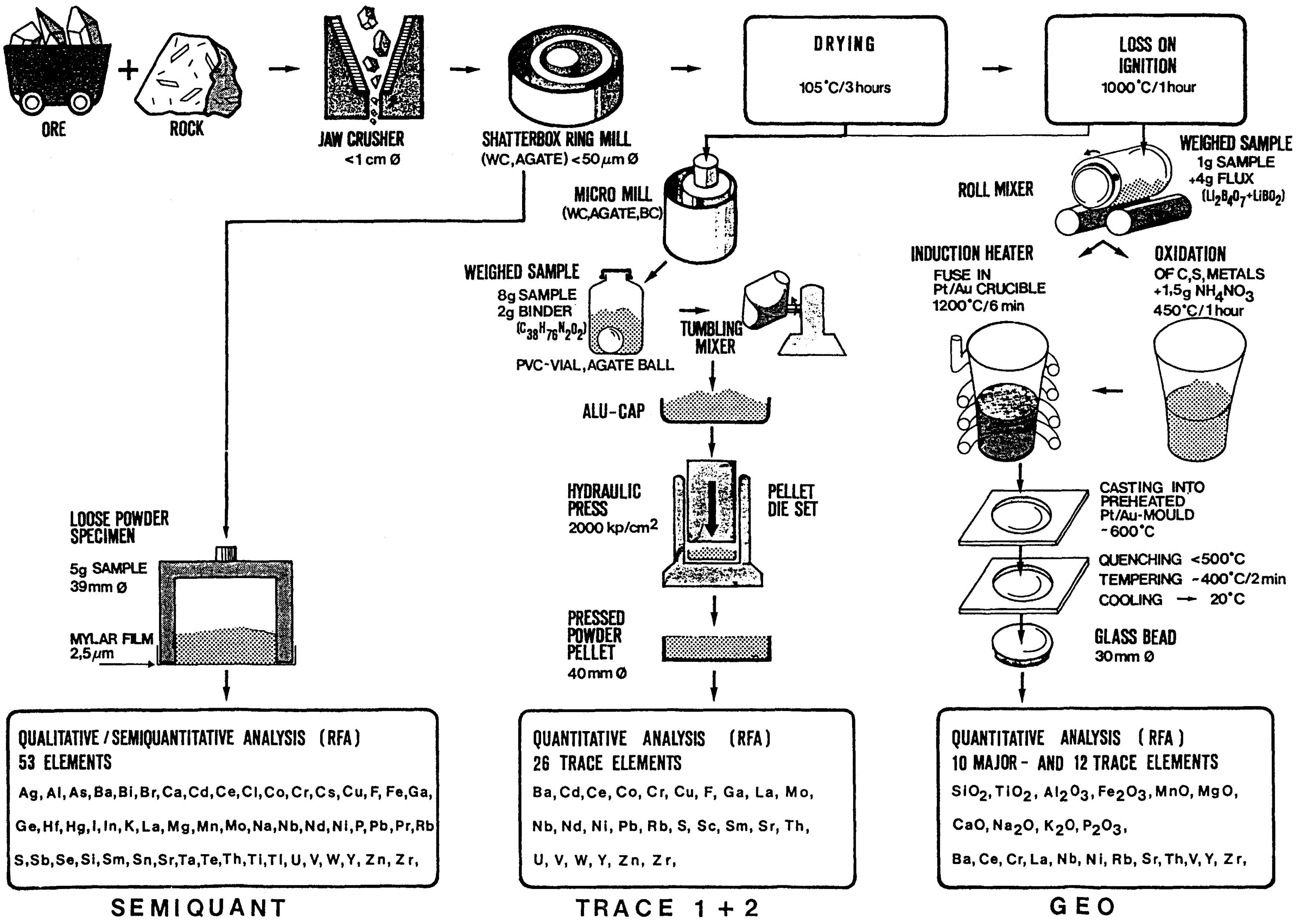

Figure 1. Flow diagram of analytical sequence for the analysis of SDO–1.

Table 1. Instrument set-up (Rh-tube) of major and trace element analyses

								Background		Time (sec)		Corrections		
Element	Line	kV	mA	Coll[1]	Crystal	D[2]	Angle	+Offset	−Offset	Peak	Bkg[3]	Bkg[3]	Lo[4]	Ir[5]
Al	Kα	40	75	C	PE	FL	144.81	—	5.00	20	4			
Ba	Lβ	50	60	C	LiF200	FL	79.22	1.34	—	120	60			
Ca	Kα	40	50	F	LiF200	FL	113.14	1.70	1.20	10	4			
Ce	Kα	100	30	F	LiF420	SC	22.81	.18	.30	150	150	x		x
Cr	Kα	50	60	F	LiF220	FL	107.10	—	1.30	60	30	x	VKα	
Fe	Kα	50	60	F	LiF200	FL	57.53	1.00	—	10	4	x		
K	Kα	50	60	F	LiF200	FL	136.71	1.20	—	20	10			
La	Lα	40	75	F	LiF220	FL	138.91	—	1.40	200	100			
Mg	Kα	40	75	C	PX-1	FL	23.45	1.00	—	30	10	x		
Mn	Kα	50	60	F	LiF220	FL	95.19	.70	—	20	10	x		
Na	Kα	40	75	C	PX-1	FL	28.29	4.00	—	30	10	x		
Nb	Kα	100	30	F	LiF220	SC	30.36	—	.90	150	150		YKαx	
Ni	Kα	50	60	F	LiF200	FL	48.67	1.08	—	100	50	x		x
P	Kα	40	75	C	GE	FL	141.00	1.50	—	20	10			
Rb	Kα	100	30	F	LiF220	SC	37.91	Ux1	Ux	150	150	x		x
Rh-comp.	Kα	100	30	F	LiF420	SC	41.89	—	2.70	60	30			
Si	Kα	40	75	C	PE	FL	109.00	2.00	—	20	4			
Sr	Kα	100	30	F	LiF220	SC	35.77	Ux1	Ux	150	150	x		x
Ti	Kα	50	60	F	LiF200	FL	86.18	—	1.00	20	10	x	BaLβ	
V	Kα	40	75	F	LiF220	FL	123.18	2.50	—	60	30	x	TiKα	
Y	Kα	100	30	F	LiF220	SC	33.82	Ux1	Ux	150	150	x	RbKα	
Zr	Kα	100	30	F	LiF220	SC	32.01	Ux1	Ux	150	150	x	SrKα	
Ux[6]	—	100	30	F	LiF220	SC	31.57	—	—	150	—			
Ux1[6]	—	100	30	F	LiF220	SC	38.64	—	—	150	—			

[1] Coll: collimator C=550-micron spacing
F=150-micron spacing

[2] D: detector FL=flow counter
SC=scintillation counter

[3] Bkg: background

[4] Lo: line overlap corrections for line interferences VKβ, YKβ, BaLα, TiKβ, SrKβ

[5] Ir: internal ratio: RhKα Compton

[6] Background Correction

Instrumentation

Analyses were performed on an automated Philips PW 1404 sequential X-ray spectrometer controlled by a DEC micro-PDP11. The PW 1404 is equipped with a 100-kV (3-kW) generator and a 12-position sample changer. A rhodium side-window tube and LiF420, LiF220, LiF200, GE, PE, and PX–1 analyzing crystals were used for the determinations (table 1).

Correction of the quantitative measurement data to compensate for drift was done using a monitor sample. A polished shoshonitic volcanic rock was prepared as monitor sample, and eight major elements (Al, Ca, Fe, K, Mg, Na, Si, Ti) in the analytical program were corrected with drift-correction factors.

Data Evaluation

For matrix correction the new Philips calculation model was applied. The Philips model is a combination of correction models (Claisse-Quintin, 1967; de Jongh, 1973; Lucas-Tooth-Pyne, 1964; and Rasberry-Heinrich, 1974). The corrections may be based on count rates, concentrations, or combinations of both. The Philips model includes terms that can be calculated or entered during the regression analyses for spectral interferences, constant background, varying background, and line overlap correction factors.

In the first step of regression analyses, theoretical alphas were used based on the fundamental parameter method (Criss and Birks, 1968; Shiraiwa and Fujino, 1966). The sample matrix, spectrometer geometry, and X-ray tube are taken into account in these theoretical alpha values. Regression analysis is considered to be more general and flexible for application to samples with wide concentration ranges. During regression analysis, the matrix correction factors (theoretical alphas) are, in part, recalculated.

For several elements (Ni, Rb, Sr, Y, Zr, Nb, Ce) the "internal ratio" method has been applied (Leoni and Saitta, 1977). This matrix correction is based on RhKα Compton scatter and corrects for absorption effects due to the major elements without the need to determine these elements (table 1).

Loss on Ignition

The rock powders were dried in an oven for 3 hours at 105°C. The dried rock powders were ignited for 1 hour at 1,000°C in a muffle furnace using platinum crucible. Loss on ignition (LOI) was determined in duplicate by igniting 1-g aliquots of sample powders.

Table 2. The program parameters for the HGA-400

Step		1	2	3	4
Temperature	°C	120	650	1900	2650
Ramp time	sec	10	10	0	1
Hold time	sec	20	30	5	3
Gas flow	mL/min			50	

Determination of Gold by Graphite Furnace Atomic Absorption Spectrometry

The determination of gold in geological samples requires its separation from the matrix. Instead of the frequently used 4-methyl-2-pentanon, the gold with palladium was extracted quantitatively by dibutyl sulfide in toluene, following a method described by Rubeska and others (1977). Besides Au and Pd, some Ag will also be extracted; whereas extraction of other elements can be neglected. A repeated treatment of geological samples with aqua regia gives 99 percent recovery of Au. Gold contents up to 0.5 μg/g should be detected by graphite furnace atomic absorption spectrometry (AAS), whereas higher contents demand flame AAS. Two portions of 10 g were taken from each bottle (bottles no. 0521 and no. 0756). The samples were dried at 110°C and then ashed for 2 hours each first at 480°C and then at 600°C, to oxidize all organic material, carbon, and sulfur. For total decomposition the samples were dissolved by HF and $HClO_4$ and then treated with aqua regia. Gold was extracted from the solutions using 0.2M dibutyl sulfide in toluene. The measurements

Table 3. X-ray fluorescence (XRF) determinations of major and trace elements in USGS Devonian Ohio Shale SDO–1

	SDO–1 B. No. 0521			SDO–1 B. No. 0756			SDO–1 B. No. 0310			SDO–1 Mean		
Element (wt%)	X (*n*=6)	RMS[1] (%)	RMS[2] (% rel.)	X (*n*=6)	RMS[1] (%)	RMS[2] (% rel.)	X (*n*=6)	RMS[1] (%)	RMS[2] (% rel.)	X (*n*=6)	RMS[1] (%)	RMS[2] (% rel.)
SiO_2	49.82	0.063	0.13	48.19	0.057	0.12	48.61	0.055	0.11	48.88	0.714	1.46
TiO_2	.69	.001	.13	.67	.003	.49	.68	.004	.64	.68	.011	1.62
Al_2O_3	12.54	.032	.25	12.15	.026	.22	12.51	.031	.25	12.40	.186	1.50
Fe_2O_{3TOT}	9.31	.012	.13	8.95	.012	.13	9.12	.007	.08	9.12	.150	1.65
MnO	.039	.001	3.59	.035	.002	4.50	.037	.001	2.75	.037	.020	5.56
MgO	1.53	.020	1.28	1.49	.008	.53	1.50	.019	1.28	1.51	.024	1.58
CaO	1.07	.008	.78	1.03	.009	.92	1.04	.006	.58	1.05	.018	1.72
Na_2O	.44	.014	3.23	.45	.014	3.15	.31	.018	5.89	.40	.067	16.79
K_2O	3.25	.019	.58	3.13	.009	.29	3.17	.011	.36	3.17	.054	1.67
P_2O_5	.11	.003	2.74	.11	.002	2.18	.11	.002	1.89	.11	.003	2.38
LOI	19.77			21.75			20.98			20.83		
Total	98.57			97.96			98.07			98.19		
	(μg/g)	(μg/g)		(μg/g)	(μg/g)		(μg/g)	(μg/g)		(μg/g)	(μg/g)	
V	162	3	2.0	156	4	2.5	156	5	3.3	158	5	3.0
Cr	63	3	4.5	65	6	8.7	66	5	7.0	65	5	6.8
Ni	93	2	2.2	92	2	1.5	94	2	2.0	93	2	2.2
Rb	135	1	.6	131	1	.5	136	1	.5	134	3	1.7
Sr	84	1	1.2	81	1	1.2	54	1	1.8	73	14	18.6
Y	47	1	1.2	47	1	2.1	29	1	2.4	41	9	21.7
Zr	175	1	.3	170	1	.3	167	1	.42	171	3	1.6
Nb	13	1	4.9	13	1	3.4	13	1	1.4	13	1	4.7
Ba	389	29	7.6	380	13	3.4	357	17	4.6	375	24	6.2
La	37	10	26.0	34	4	9.8	37	6	14.9	36	7	18.0
Ce	84	20	24.4	71	7	10.3	92	12	12.6	82	16	19.4

[1] RMS: root mean square (standard deviation)

[2] RMS (% rel): percentage relative root mean square

Table 4. Coulometric determinations of C_{tot}, C_{carb}, C_{org}, and S in USGS Devonian Ohio Shale SDO–1

	SDO–1 B. No. 0521			SDO–1 B. No. 0756			SDO–1 B. No. 0310			SDO–1 Mean		
Element (wt%)	X (n=6)	RMS[1] (%)	RMS[2] (% rel.)	X (n=6)	RMS[1] (%)	RMS[2] (% rel.)	X (n=6)	RMS[1] (%)	RMS[2] (% rel.)	X (n=6)	RMS[1] (%)	RMS[2] (% rel.)
C_{tot}	10.34	0.061	0.59	9.70	0.025	0.26	9.97	0.086	0.86	10.03	0.288	2.87
C_{carb}	.30	.013	4.33	.15	.004	2.67	.23	.004	1.74	.23	.066	28.70
C_{org}	10.04	.063	.63	9.55	.026	.27	9.74	.090	.92	9.80	.226	2.31
	(n=5)			(n=4)			(n=9)			(n=18)		
S	5.23	.071	1.36	5.10	.022	.43	5.18	.016	.31	5.17	.062	1.20

[1]RMS: root mean square (standard deviation)

[2]RMS (% rel): percentage relative root mean square

Table 5. Results for gold after fire assay preconcentration

10-g run	Au (μg/g)	25-g run	Au(μg/g)
SDO–1 bottle no. 0521	<0.005	SDO–1 bottle no. 0521	0.004
	.01	SDO–1 bottle no. 0756	<.003
SDO–1 bottle no. 0756	<.005		
	.008		

were made using a Perkin Elmer HGA-400 graphite furnace in combination with a Zeiss FMD 4 atomic absorption spectrometer. The program parameters for the HGA, from Konopasek and others (1988), are given in table 2.

Determination of CARBON$_{\text{total}}$, CARBON$_{\text{carbonate}}$, CARBON$_{\text{organic}}$, and SULFUR by Coulometric Titration

The carbon analyses were made following the method of Herrmann and Knake (1973). The sulfur determinations were done by adopting the method published by Lange and Brumsack (1977). For each run, portions of 100 g were taken from the bottles no. 0521, no. 0756, and no. 0310. To measure the total carbon content, 100 mg of each sample were ignited without additional reagents in an oxygen current at about 1,250°C. The carbonate carbon content was determined by dissolving 100 mg of each sample in orthophosphoric acid and measuring the evolved CO_2. The organic carbon content was calculated by difference.

To measure the sulfur content, 100 mg of each sample were mixed with 500 mg of V_2O_5 and 500 mg of Fe and ignited at 1,380°C. The analyses were performed on a Ströhlein Coulomat 702/SO/CS/E. The SO_2 released is absorbed in a Na_2SO_4 solution (10 g Na_2SO_4 in 200-mL doubly distilled water to which 2 mL of 30-percent H_2O_2 had been added), lowering its pH. Again the pH is returned to its starting point by electrolysis. The amount of energy required is equivalent to the quantity of SO_2 absorbed.

CONCLUSIONS

Analytical data from all XRF determinations are presented in table 3, and analytical data for coulometric titrations to determine C and S are presented in table 4. Gold data in table 5 show inhomogeneous distribution of gold in 10-g samples. Because only a single repeat analysis from each bottle at 25-g sample sizes was possible, homogeneity could not be assessed based on the larger sample weight. These results also appear in the table.

Precisions for MnO, Na_2O, and P_2O_5 within bottle are larger than expected based on past experience with the method. As a result, between-bottle analysis of variance shows no significant difference despite suspected inhomogeneity cited in Kane and others (1990). Similar inability to assess material in inhomogeneity because of large within-bottle imprecision affects the measurement for several trace elements (Cr, Sr, Y, Ba, La, and Ce).

As figure 2 shows, the measured mean values (n=18) presented in table 2 fit well within the range of confidence (± standard deviations) of the recommended average values for SDO–1 published by Kane and others (1990). Mean values of Fe_2O_3, K_2O, Nb, and Rb do not plot exactly within the confidence range shown; however, expansion of that range to ± two standard deviations does encompass those values (fig. 1); therefore, it can be concluded that the analytical methods (XRF, AAS, and coulometry) used are satisfactory, reliable tools for solving analytical problems related to the geochemistry of black shales.

[%]		Width of confidence interval		Recommended values			
SiO_2		48.65	*48.88*	49.28		49.91	
Al_2O_3		12.04		12.27	*12.40*	12.50	
Fe_2O_3	*9.12*	9.13		9.34		9.55	
CaO		1.00	*1.05*	1.05		1.10	
MgO		1.50	*1.51*	1.54		1.58	
Na_2O		.35		.38	*.40*	.41	
K_2O	*3.17*	3.29		3.35		3.41	
P_2O_5		.10	*.11*	.11		.12	
TiO_2		.68	*0.68*	.71		.74	
MnO		.037	*.037*	.042		.047	
LOI		20.8	*20.8*	21.7		22.6	
S		4.91	*5.17*	5.35		5.79	
C_{tot}		9.51		9.95	*10.03*	10.39	
C_{org}		9.23		9.68	*9.80*	10.13	
[µg/g]							
Au		(0.002			*0.0035*	0.0035)	
Ba		359	*375*	397		435	
Ce		71		79	*82*	87	
Cr		59	*65*	66		74	
La		34	*36*	39		43	
Nb		10.2		11.4		12.6	*13.0*
Ni		90	*93*	100		109	
Rb		122		126		130	*134*
Sr		64	*73*	75		86	
V		139	*158*	160		181	
Y		34	*41*	41		47	
Zr		141		165	*171*	189	

Figure 2. Recommended average values for SDO–1 (central column) and their ranges of confidence (± standard deviation) (Kane and others, 1990) in comparison to the mean values as reported in tables 3 and 4 (italicized and underscored).

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Chapter C

Inductively Coupled Plasma Determination of Nine Rare Earth Elements in the USGS Devonian Ohio Shale SDO–1

By IWAN ROELANDTS

U.S. GEOLOGICAL SURVEY BULLETIN 2046

THE USGS REFERENCE SAMPLE DEVONIAN OHIO SHALE SDO–1

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Inductively Coupled Plasma Determination of Nine Rare Earth Elements in the USGS Devonian Ohio Shale SDO–1

By Iwan Roelandts[1]

Abstract

The U.S. Geological Survey Devonian Ohio Shale SDO–1 has been analyzed for nine of the rare earth elements (REE) by inductively coupled argon plasma atomic emission spectrometry (ICP–AES). Triplicate portions from two bottles of the material were analyzed in random order to estimate analytical precision and test for homogeneity. The precision, based on the samples analyzed, is generally better than 1 percent. The one-way analysis of variance was used with our ICP determinations; no evidence for differences in REE concentrations between these two randomly selected bottles was observed.

INTRODUCTION

Nine of the rare earth elements (REE) in the U.S. Geological Survey (USGS) Devonian Ohio Shale SDO–1 were determined by inductively coupled plasma atomic emission spectrometry (ICP–AES) following cation-exchange separation. Two bottles randomly selected from the stock were received and three separate portions from each bottle were analyzed to provide a one-way experimental design using the two bottles as the single variable of classification. The six portions were analyzed in random order.

The REE have been found to be extremely useful in several studies of sedimentary processes (weathering, transport, and diagenesis). Very few years ago, instrumental neutron activation analysis (INAA) and isotope dilution mass spectrometry (IDMS) were the only sensitive and accurate techniques in use for geochemical REE analysis. ICP–AES is rapidly becoming an established analytical method for the determination of REE, especially when large numbers of samples of common silicate rocks must be analyzed. This technique has several advantages, the principal of which are low detection limits, good precision and accuracy, low sample matrix effects, speed of analysis, and wide linear dynamic concentration range.

ICP spectra of rock samples are not simple; a very large number of emission lines are present. To avoid interference from other elements and thereby improve accuracy and detection limits, some workers chemically separated the REE as a group from the rock matrix, in most cases by an ion-exchange procedure (for example, Walsh and others, 1981; Brenner and others, 1981, 1984; Crock and Lichte, 1982; Bolton and others, 1983; Yoshida and others, 1983; Crock and others, 1984, 1986; Aulis and others, 1985; Jarvis and Jarvis, 1985, 1988; Roelandts and Michel, 1986; Roelandts, 1988a; Roelandts, 1990; Govindaraju and Mevelle, 1987; Zachman, 1988; Sulcek and others, 1989; Watkins and Nolan, 1990).

In this work a separation of the REE from the other constituents after an acid decomposition of the sample was achieved using the strong acid-type resin Dowex 50WX8. The REE were first held quantitatively on the cationic resin during the initial washing with 1.75*M* hydrochloric acid to remove unwanted elements and then desorbed using 8*M* nitric acid as an eluent. The experimental conditions of this separation procedure have been previously determined (Roelandts, unpub. data, 1975).

EXPERIMENT PARAMETERS

Apparatus

ICP Equipment

A Bausch and Lomb model 3510 sequential ICP spectrometer (Applied Research Laboratories) operated at 1.2 incident kW was used for this study. A DEC PDP–11 computer controlled all instrument functions. The plasma gas-flow and the coolant gas-flow rates were 0.8 and 12.0 L/min, respectively. A concentric Meinhard type nebulizer was employed, and the sample solution uptake was fixed at 3 mL/min. The observation height was 15 mm above the load coil. Further details on the instrumentation are

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available elsewhere (Roelandts and Michel, 1986; Roelandts, 1988a).

Cation-Exchange Columns

Borosilicate glass tubes of 10-mm internal diameter filled with Dowex 50X8 cation-exchange resin (6-g dry weight) were used as columns. The settled resin height in the column was adjusted to 200 mm. Before starting the separation, the columns were equilibrated by passing 50 mL of 1.75*M* hydrochloric acid through them.

Reagents

Cation-Exchange Resin

The resin used was the Dowex 50X8 sulphonated cation exchanger (hydrogen form, 100 to 200 mesh) supplied by Fluka Co., Buchs, Switzerland. Before use, the fine particles were removed by several decantations.

Rare Earth Elements Standard Solutions

Individual REE solutions (1,000 μg/mL) were prepared by dissolving high purity (99.9 percent) REE oxides (Rare-Earth Products Ltd., London, U.K.) in hot nitric acid. Before weighing, the oxides were heated at 95°C.

The single-element solutions were prepared by appropriate dilution of the stock solutions. All solutions were stored in polypropylene bottles having a total nitric acid content of 5 percent by volume.

Chemicals

All the acids used were analytical-reagent grade.

Analytical Procedure

Dissolution of the Samples

Samples 1-g each were digested on a water-bath using hydrofluoric-nitric acid attack and evaporated to dryness. The salts were dissolved in concentrated hydrochloric acid by heating. The solutions were again evaporated to dryness. The HCl digestion was repeated at least twice. Finally, the residues were dissolved in 1.75*M* HCl.

Cation-Exchange Separation

The 1.75*M* HCl sample solution was passed through the preequilibrated resin column. After the elution of iron, calcium, and other unwanted matrix elements with 100 mL of 1.75*M* HCl, the REE adsorbed on the column were washed out with 75 mL 8*M* HNO_3. All separations were done at an eluent flow rate of about 1 mL/min. Six separate exchange experiments were performed simultaneously.

The REE eluate was then evaporated to dryness, dissolved in 5-percent (*V/V*) nitric acid, and diluted to 25 mL. This solution was stored in a polypropylene bottle until the ICP–AES measurements were carried out.

Table 1. Spectral interference correction coefficients

Element	Wavelength (in nanometers)	Interfering rare earth elements and correction coefficients	
La	398.852		
Ce	418.660		
Nd	430.358		
Sm	359.260	Nd (0.0372)	Gd (0.0313)
Eu	381.967	Nd (0.0040)	
Gd	342.247	Ce (0.0037)	
Dy	353.170	Nd (0.0012)	
Yb	328.937		
Lu	261.542		

ICP–AES Measurements

For each sample solution nebulized into the plasma, a stabilization time was set at 30–s ("preflush time") and followed by three 1–s signal integrations; the sample intensities were calculated as the arithmetic mean of these three readings. External calibration was made using single-element solutions of REE (in 5-percent (*V/V*) nitric acid). A 5-percent (*V/V*) nitric acid solution was used to determine the true background under the peak. All intensities were corrected for background so obtained.

After the cation-exchange separation procedure, the only important spectral interferences that remained were those caused by overlap from other REE peaks. The REE analytical lines selected in this work are listed in table 1. The choice is a compromise between signal intensity and relative freedom from spectral interferences. Spectral profiles of these lines and correction coefficients for mutual REE interferences have been previously reported (Roelandts and Michel, 1986). They are largely dependent on the resolution of the spectrometer and may vary from instrument to instrument. A wavelength scan 0.1 nanometer (nm) on each side of the Sm emission line at 359.260 nm (10 μg/mL Sm; 100 μg/mL for other REE) is illustrated in figure 1. Overlap corrections introduced in this study are indicated in table 1. For example, a sample that contains 1 μg/g Nd generates the equivalent of 0.0372 μg/g Sm; therefore, the contributions from Nd to Sm will be estimated by multiplying the Nd concentrations by 0.0372 and subtracting this product from the total measured Sm content.

RESULTS AND DISCUSSION

Three portions from the two bottles of SDO–1 were analyzed in random order for nine REE (La, Ce, Nd, Sm, Eu, Gd, Dy, Yb, and Lu). The experimental results of the individual samples (average of three measurements on the

Table 2. Determination of nine rare earth elements in USGS Devonian Ohio Shale SDO–1

[All concentrations in μg/g]

Element	Bottle 0189			Bottle 0717			Mean
	Determination			Determination			
	A	B	C	A	B	C	
La	36.2	35.6	35.6	36.0	35.9	36.0	35.9
Ce	76.9	75.3	75.3	77.6	76.7	74.9	76.1
Nd	37.9	38.0	38.7	38.5	38.1	38.3	38.3
Sm	7.7	7.6	7.5	7.7	7.6	7.6	7.6
Eu	1.64	1.66	1.65	1.65	1.67	1.69	1.66
Gd	7.8	7.6	7.8	7.8	7.9	7.9	7.8
Dy	6.1	6.0	6.0	6.1	6.1	6.1	6.1
Yb	3.05	2.99	3.00	3.04	3.09	3.08	3.04
Lu	.45	.44	.44	.45	.45	.47	.45

solution) are presented in table 2, including the mean of the six separate analyses. Based on these analyses, precision is estimated to be better than 1 percent.

The one-way analysis of variance was used with the ICP data to determine if the bottles are homogeneous with respect to REE content. Table 3 summarizes the calculations and the conclusions from the analysis of variance. The F ratio calculated for REE in no case exceeds the allowable value $F_c(0.95)(1,4)=7.7086$ as shown in the F tables. Therefore, the statistical analysis demonstrated that SDO–1 may be considered homogeneous for the elements specified at the 95-percent confidence level. Because of the random selection of the bottles for the experiment, this conclusion may be extrapolated to the entire lot of bottles.

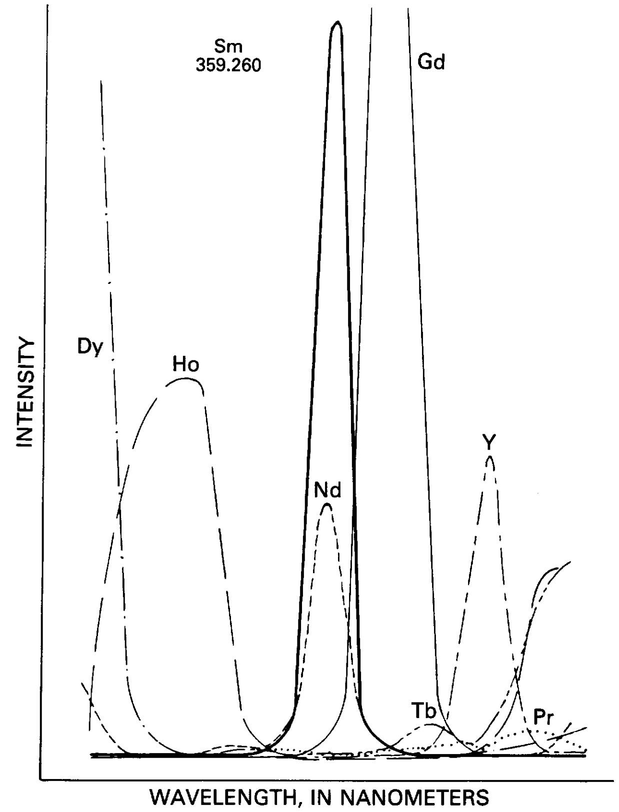

Figure 1. Wavelength scan of the Sm 359.260-nanometer line (10 μg/mL Sm; 100 μg/mL for other rare earth elements).

In table 4, the average REE concentrations obtained in the present work (bottle 0717) are compared with results for one analysis of this sample previously undertaken in our laboratory about 18 months ago. The agreement between these two sets of data is judged to be excellent and reflects the long-term reproducibility that can be achieved using the outlined method. Additionally, from this table it can be seen that our determinations compare favorably with the ICP–AES values reported by Crock and others (1986) and with the final recommended concentrations (Kane and others, 1990).

The accuracy of our ICP–AES method has been established by performing analyses on more that 40 different international geochemical reference materials (Roelandts and Michel, 1986; Roelandts, 1987, 1988a, 1988b, 1989) and through participation in a series of collaborative

Table 3. One-way analysis of variance

[d.f., degree of freedom; NS, not significant]

Element	Mean squares		F–ratio	Conclusion
	d.f.=1	d.f.=4		
La	0.04167	0.06167	0.6757	NS
Ce	.48167	1.37167	.3512	NS
Nd	.01500	.11500	.1304	NS
Sm	.00167	.00667	.2500	NS
Eu	.00060	.00025	2.4000	NS
Gd	.01000	.02000	.5000	NS
Dy	.00667	.00167	4.0000	NS
Yb	.00482	.00087	5.5577	NS
Lu	.00027	.00008	3.2000	NS

Table 4. Results obtained for USGS Devonian Ohio Shale SDO-1 in the present work compared with previous ICP data

[All concentrations in μg/g; ICP, inductively coupled plasma]

Element	This work[1]	Previous work[1,2]	Crock and others, 1986	Average[3]
La	36.0	35.9	35.6	*38.5±4.4
Ce	76.4	76.2	71.8	*79.3±7.8
Nd	38.3	38.2	36.3	36.6±3.3
Sm	7.6	7.6	7.6	7.7±0.81
Eu	1.67	1.68	1.65	1.6±0.22
Gd	7.8	7.8	7.8	7.4±1.9
Dy	6.1	5.9	6.1	*6.0±0.65
Yb	3.07	3.04	3.11	*3.4±0.46
Lu	.46	.45	.44	.54±0.14

[1] Bottle 0717

[2] Roelandts, 1988b

[3] Kane, table 1, p. 2, this volume

*recommended (all others are compilation averages)

Table 5. Determination of nine rare earth elements in USGS sedimentary reference samples

[All concentrations in μg/g; ICP, inductively coupled plasma]

	MAG-1 Marine mud[1]		SCO-1 Code Shale[2]		SDC-1 Mica schist[3]		SGR-1 Green River Shale	
Element	ICP[4,5]	Consensus value[6]	ICP[4,5]	Consensus value[6]	ICP[4,5]	Consensus value[6]	ICP[4,5]	Consensus value[6]
La	42.6	43±4	29.1	29.5±1.1	42.6	42±3	18.6	20.3±1.8
Ce	90.2	88±9	59.0	62±6	95.2	93±7	33.8	36±4
Nd	38.3	38±5	26.0	26±2	41.2	40±4	14.8	15.5±1.7
Sm	7.4	7.5±0.6	5.5	5.3±0.3	8.3	8.2±0.5	2.1	2.7±0.3
Eu	1.48	1.55±0.14	1.12	1.19±0.12	1.67	1.71±0.12	.41	.56±0.09
Gd	5.8	5.8±0.7	4.0	4.6±0.7	6.7	7.2±0.4	2.21	2.0±0.4
Dy	4.8	5.2±0.3	3.7	4.2±0.5	6.4	6.7±0.9	1.82	1.9±0.3
Yb	2.82	2.6±0.27	2.28	2.27±0.24	3.9	4.0±0.7	.96	.94±0.16
Lu	.39	.40±0.04	.33	.338±0.033	.50	.53±0.11	.17	.14±0.03

[1] Manheim, and others, 1976

[2] Schultz, and others, 1976

[3] Flanagan and Carroll, 1976

[4] Roelandts, 1987

[5] Roelandts, 1988a

[6] Gladney and Roelandts, 1988

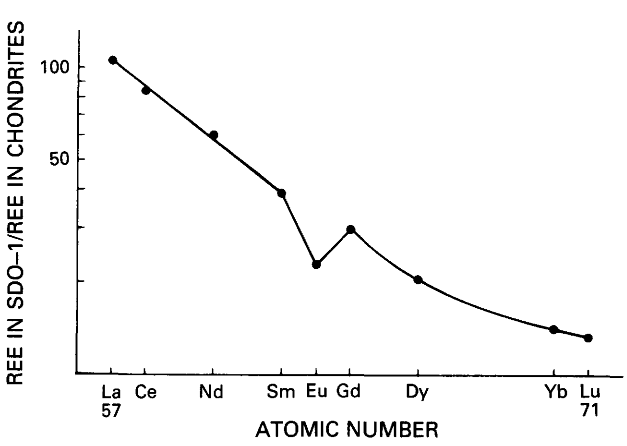

Figure 2. Chondrite-normalization pattern for the Devonian Ohio Shale SDO—1.

studies. Good agreement between our ICP determinations and the preferred values for these reference materials is observed in most cases. Table 5 contains results of nine REE in USGS sedimentary reference samples. Comparison of our ICP values with the consensus values calculated by Gladney and Roelandts (1988) indicates an accuracy of ±4 percent. The absence of any serious systematic bias in our REE determinations is also evident and shows the validity of the analytical procedure.

The chondrite normalized concentrations for SDO–1 are plotted against the atomic number in figure 2 using the chondrite values reported by Laul and Rancitelli (1977). This procedure offers a quick evaluation of the quality of data for REE abundances. A smooth curve that is widely accepted as a quality criterion for REE analysis can be observed in our case.

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Chapter D

Instrumental Neutron Activation Analysis of Devonian Ohio Shale SDO–1

By GREGORY A. WANDLESS

U.S. GEOLOGICAL SURVEY BULLETIN 2046

THE USGS REFERENCE SAMPLE DEVONIAN OHIO SHALE SDO–1

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FIGURES

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Instrumental Neutron Activation Analysis of Devonian Ohio Shale SDO–1

By Gregory A. Wandless

Abstract

The U.S. Geological Survey geochemical reference sample Devonian Ohio Shale SDO–1 was analyzed by instrumental neutron activation analysis. The relatively high uranium concentration in SDO–1 caused several isotopic and spectral interferences that had to be resolved. Special data processing techniques were applied to the assay of lutetium to remove spectral interferences from uranium, and significant corrections had to be applied to several elements for fission product interferences. A correction for the ruthenium fission product interference has been made to barium since the publication of the original SDO–1 compilation, resulting in a significant improvement in accuracy. Four replicates from two randomly selected bottles were analyzed; and the precision was estimated to be 5 percent or better for a majority of elements, and the accuracy was demonstrated by no rejection of data in the determination of "recommended values." Analysis of variance shows no significant variation between bottles.

INTRODUCTION

A discussion of the purpose for collecting SDO–1, sample description and preparation, and the analytical program have already been presented (Kane and others, 1990). Applying instrumental neutron activation analysis (INAA) to the analysis of SDO–1 provides an efficient means for characterization because the method can provide precise data for approximately 30 major, minor, and trace elements in a single sample aliquot without chemical treatment. The underlying principles and the application of INAA to geologic samples have been described numerous times (Gordon and others, 1968; Hertogen and Gijbels, 1971; Baedecker and others, 1977; Jacobs and others, 1977; Laul, 1979; Baedecker and McKown, 1987). The most significant problems associated with the analysis of SDO–1 will be discussed in detail.

EXPERIMENT PARAMETERS

The samples of SDO–1 as received for analysis needed no further treatment for activation analysis. Four aliquots of SDO–1 from each of two bottles, two multielement standards, a standard for calcium and titanium, and the U.S. Geological Survey (USGS) geochemical reference sample SGR-1, all weighing approximately 0.5 g, were weighed into 2/5-dram polyethylene vials. The vials were heat sealed, placed in a polyethylene bag, and packed into an aluminum can for irradiation.

Samples and standards were irradiated simultaneously for 8 hours in the A-2 position of the Texas A&M reactor facility, providing a neutron flux of 2×10^{12} neutrons $\mathrm{cm}^{-2}\mathrm{s}^{-1}$. After irradiation, the samples were returned after decaying for 7 days. The vials were then unpacked, washed externally with water and alcohol, and placed in clean 2-dram polyethylene vials for counting.

Samples and standards were counted on coaxial, high-purity germanium (HPGe) and low-energy photon detectors (LEPD) 7 days after irradiation for 1 hour each, after 14 days on a HPGe for 1 hour, and again on the HPGe and LEPD after 2 months for 2 hours. Gamma-ray spectra were acquired on a Nuclear Data 6700 multichannel analyzer and transferred to a VAX 11/780 for data reduction. Spectra were analyzed using the SPECTRA program (Baedecker and Grossman, 1989).

RESULTS

Results for the eight replicate analyses of SDO–1 are given in table 1. Means and standard deviations were computed assuming no between-bottle variance. The precision for the majority of elements is 5 percent or better, and only two (Ti and Zr) have a coefficient of variation of greater than 10 percent. With regard to accuracy, it is noted that only data for barium were rejected during the initial determination of "recommended values" or averages for the SDO–1 standard. Since the initial analysis, corrections for fission-product interference on barium have been determined and have improved the accuracy of the barium data such that those results can now be included in the derivation of recommended values. To evaluate sample homogeneity

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Table 1. Instrumental neutron activation analysis results for USGS geochemical reference sample SDO–1

	Bottle 699				Bottle 761					
	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Mean	Standard deviation
Na (wt. %)	0.266	0.269	0.269	0.269	0.264	0.272	0.269	0.269	0.268	0.0024
K	2.76	2.71	2.65	2.71	2.67	2.82	2.66	2.68	2.71	.050
Ca	<12	<12	<11	<11	<14	<14	<11	<11	—	—
Ti	<.7	<.6	.82	<.9	.53	<.6	.62	<.6	.66	.150
Fe	6.56	6.59	6.53	6.56	6.40	6.50	6.58	6.61	6.54	.067
Sc (μg/g)	12.4	12.6	12.3	12.4	12.1	12.3	12.4	12.4	12.4	.140
Cr	62.7	64	63	64.5	62.5	64.3	64.6	63.5	63.6	.83
Co	45.0	45.3	44.2	44.6	43.7	44.3	45.1	44.9	44.6	.54
Ni	95	101	83	92	86	86	100	91	92	6.6
Zn	62	65	61	61	60	58	58	63	61	2.36
As	63.0	63.2	61.9	63.4	62.7	62.7	62.6	62.4	62.7	.47
Se	7.3	6.3	<5	6.6	<5	<8	<8	<5	6.7	.51
Rb	127	133	129	129	125	130	125	126	128	2.80
Sr	<230	138	140	140	158	140	130	140	141	8.4
Zr	124	<260	100	140	102	84	160	<130	118	28.4
Mo	123	126	127	129	125	126	124	127	126	1.90
Sb	4.66	4.66	4.62	4.52	4.37	4.48	4.68	4.68	4.58	.115
Cs	6.41	6.46	6.39	6.56	6.29	6.44	6.42	6.38	6.42	.070
Ba	404	383	409	397	394	413	423	406	403	12.3
La	33.1	33.6	33.2	33.6	33.0	33.1	33.1	33.4	33.3	.240
Ce	69.7	72.2	69.5	70.9	68.6	70.4	70.8	70.6	70.3	1.08
Nd	31	33	31	33	32	33	33	33	32	.80
Sm	7.56	7.73	7.68	7.78	7.60	7.60	7.60	7.69	7.66	.070
Eu	1.46	1.51	1.44	1.48	1.44	1.47	1.47	1.46	1.47	.0220
Tb	1.13	1.17	1.20	1.17	1.13	1.10	1.18	1.13	1.15	.030
Yb	3.43	3.42	3.38	3.47	3.27	3.25	3.49	3.40	3.39	.080
Lu	.48	.49	.48	.50	.47	.47	.47	.48	.48	.0110
Hf	4.43	4.46	4.38	4.37	4.27	4.39	4.38	4.37	4.38	.050
Ta	1.10	1.08	1.07	1.09	1.06	.99	1.07	1.09	1.07	.030
Th	9.65	9.91	9.70	9.85	9.60	9.71	9.86	9.85	9.77	.115
U	40.4	41.2	41.3	40.8	40.4	40.4	40.5	41.0	40.8	.38

for the elements determined by INAA, an analysis of variance was performed on the data, and the F–statistic was tabulated in table 2. Since the critical F–value for the given degrees of freedom was not exceeded in any case, the hypothesis that there is no significant variation between bottles is accepted.

DISCUSSION

Baedecker and McKown (1987) give a detailed description of the factors that can affect the precision and accuracy of INAA; and for the majority of the trace elements determined in SDO–1, those factors were accounted for or insignificant during the analysis. For example, errors due to poor counting statistics were unimportant because of the relatively high count rates obtained during the analysis of SDO–1. However, the relatively high concentration of uranium (40 μg/g) introduced two forms of interferences that required evaluation for their effects on the analysis of SDO–1.

During neutron irradiation, ^{235}U and ^{238}U undergo fission, producing a host of daughter products called fission products. Some of these fission products are identical to the indicator radionuclides produced by the neutron irradiation of certain trace elements in SDO–1 (isotopic interference). Others have gamma-ray lines close to the lines of interest (spectral interferences). Failing to correct for these interferences will produce anomalous results for some elements. There are seven trace elements determined by INAA that can have significant interferences from uranium-fission products: Ba, Mo, Zr, La, Ce, Nd, and Sm. Corrections for the isotopic interference from fission products can be determined by theoretical calculations or by irradiating a known quantity of uranium and measuring the quantity of those elements produced. The analytical data can then be corrected based on a determination of the concentration of uranium in the sample using the 277 keV gamma-ray from ^{239}Np. Table 3 gives the correction factors used in this study that are consistent with the recent review of the available literature of fission-product corrections used in activation analysis (Landsberger, 1989).

Table 2. Analysis of variance results for INAA of SDO–1.
[*F*–critical (95%) for Sr 6.6079, Zr 7.7087, all others 5.9874; —, insufficient data]

Element	F–statistic
Na	0.019
K	<.001
Ca	—
Sc	1.979
Ti	—
Cr	.077
Fe	.597
Co	.481
Ni	.160
Zn	2.605
As	.645
Se	—
Rb	3.000
Sr	.148
Zr	.054
Mo	.284
Sb	.557
Cs	2.063
Ba	1.673
La	2.042
Ce	.349
Nd	3.138
Sm	1.548
Eu	.665
Tb	2.195
Yb	1.447
Lu	2.864
Hf	2.704
Ta	2.053
Th	.067
U	1.947

Table 3. Fission product correction factors (apparent μg/g element/μg/g U)

^{95}Zr	11.3
^{99}Mo	.85
^{141}Ce	.29
^{147}Nd	.23
^{153}Sm	.00008
^{140}La	.002693 [exp (0.01497 t_d)−1.0]
^{131}Ba	2.8 [exp (0.0402 t_d)]

The determination of barium is complicated by the presence of fission product ^{103}Ru. The 497.1 keV line from ^{103}Ru interferes with the principle gamma-ray of ^{131}Ba at 496.4 keV. The half-life of ^{131}Ba is 12 days and of ^{103}Ru is 39.4 days; therefore, the longer the delay in counting for ^{131}Ba, the more significant is the interference from ^{103}Ru. Since no suitable interference-free line of ^{103}Ru is available to compute a correction factor for spectral interference, the factor was determined by irradiating an aliquot of uranium standard and determining the amount of ^{103}Ru produced by uranium fission. This time-dependent correction can then be applied after determination of the uranium abundance. In the initial compilation of SDO–1 analysis (Kane and others, 1990), a correction for this interference had not been applied, and the results from the 124 keV line in the first planar count were unacceptable. In this work, the correction has been applied to the barium results determined using the 496 keV line, and the agreement of the corrected results with "recommended values" is significantly improved. In an earlier compilation of SDO–1 (Kepferle and others, 1985), the barium data also suffer from the same fission-product interference.

Unlike the spectral interference from a different nuclide produced by uranium fission, the interferences to Mo, Zr, La, Ce, Nd, and Sm are caused by the formation of the indicator radionuclides of those elements by uranium fission. The correction factors for these element were determined both experimentally and theoretically by calculation (Baedecker and McKown, 1987). The interference correction to La is complicated because the fission of uranium produces the 12.8 d ^{140}Ba isotope that then decays to the 40.3 h ^{140}La. Therefore, the amount of interference is dependent upon the growth and decay of ^{140}La during the delay time, t_d, between irradiation and counting. The corrections to the La abundances were made using the time-dependent equation in table 3. The constants were determined using the Bateman equation.

All these corrections are applicable to the neutron activation analysis of a material containing uranium, and even in geochemical samples containing "normal" relative concentrations of uranium, the interference from fission products can be significant. For example, the SGR-1 sample included in this study required a 16-percent correction to Mo values and 2.6-percent and 4-percent corrections to the La and Ce data, respectively. The high relative concentration of U in SDO–1 produced corrections of 30 percent for Mo and Nd and 11 percent and 16 percent for La and Ce, respectively; and the apparent concentration of Zr due to fission products was 600 μg/g.

Spectral interferences from the high uranium content also complicated the determination of Lu. The 209.8 keV gamma-ray line of ^{239}Np, an activation product of ^{238}U, is 1.4 keV away from the principal gamma-ray line of ^{177}Lu used to assay Lu. The resolution of the HPGe detectors used was approximately 1.2 keV in this region (1.85 keV FWHM at the 1332 keV line of Co); and because complete resolution of the uranium peak from the assay peak for Lu is not possible, a doublet results. If the U/Lu ratio is small, the interference on Lu by U is small and can be determined using other uranium lines and the known intensity ratios. However, as the U/Lu ratio increases, the size of the uranium peak increases, and the determination of Lu becomes increasingly difficult. The doublet produced by U (^{239}Np) and Lu for SDO–1 is shown in figure 1. The relative

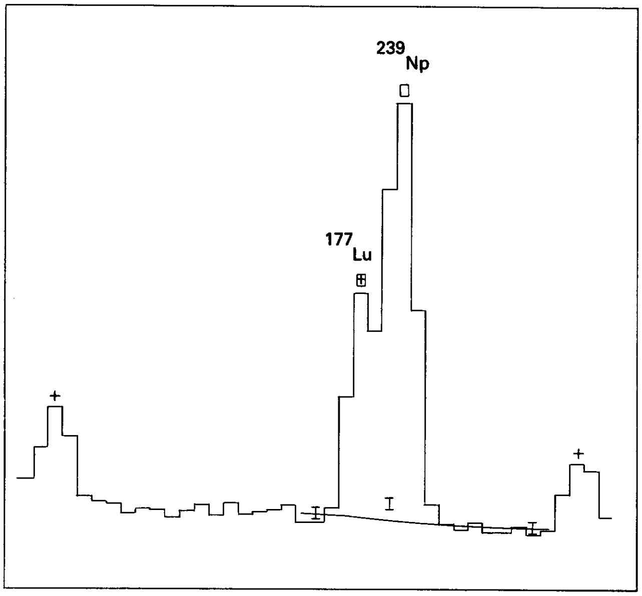

Figure 1. The Lu/U(Np) doublet prior to interactive fitting.

concentrations of U and Lu in SDO–1 still permitted the determination of Lu by performing interactive graphic plotting and fitting of the pair as described by Grossman and Baedecker (1986). Figure 2 shows the results of fitting and the residuals of the fit. Agreement between the 7- and 14-day counts suggests that the fitting routine successfully determined the peak areas for Lu and U. The accuracy of the Lu data is often evaluated by looking at the relative positions of Yb and Lu in a chondrite normalized plot of rare earth abundances. Figure 3 shows such a plot, and the smooth transition from Yb to Lu indicates high-quality Lu data.

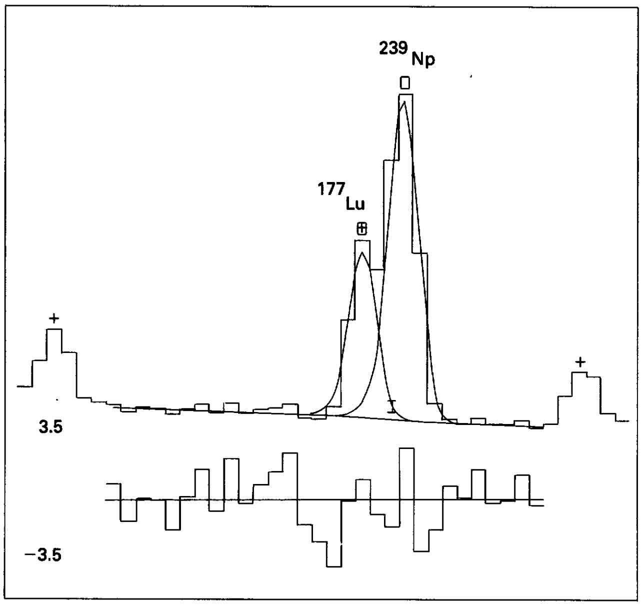

Figure 2. The Lu/U(Np) doublet after interactive fitting.

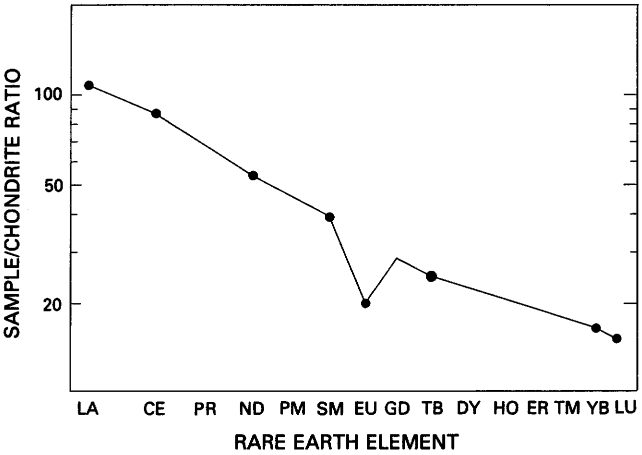

Figure 3. Chondrite normalized rare earth plot of SDO–1.

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Chapter E

Relation Between Volatile Components and Loss on Ignition as Applied to the Analysis of USGS Reference Devonian Ohio Shale SDO–1 and Rare Earth Element Analyses

By MIROSLAV HUKA and IVAN RUBESKA

U.S. GEOLOGICAL SURVEY BULLETIN 2046

THE USGS REFERENCE SAMPLE DEVONIAN OHIO SHALE SDO–1

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Relation Between Volatile Components and Loss on Ignition as Applied to the Analysis of USGS Reference Devonian Ohio Shale SDO–1 and Rare Earth Element Analyses

By Miroslav Huka *and* Ivan Rubeska[1]

Abstract

In organic-rich shales, hydrogen bound to hydrocarbons is oxidized to water and measured together with constitutional water, H_2O^+. The amount of hydrogen released from the organic matter may be assessed from the difference between the experimental loss on ignition, after correction for oxidation of ferrous iron and pyritic sulfur, and the sum of the experimentally measured volatile components, that is, sulfur, organic carbon (C_{org}), CO_2, and the measured H_2O^+. This approach has been applied to the analytical data for the reference shale SDO–1 to improve the overall summation of major constituents, which should total 100±1 percent. Results for the rare earth elements determined by inductively coupled plasma atomic emission spectrometry (ICP–AES), after two different separation procedures, are also presented. All results for SDO–1 in this report were included in the compiled data base from which recommended concentrations were derived.

INTRODUCTION

Chemical analysis of shales rich in organic matter for the major components included in a typical "silicate analysis" presents certain difficulties in achieving the expected summation to approximately 100 percent. These difficulties are caused mainly by the fact that oxygen, one of the main constituents, is not determined independently. Instead, the oxygen content is calculated on the basis of the assumptions that the standard oxide representation of the cations is correct and that the volatile components can be either accurately measured or reasonably estimated from loss on ignition (LOI). The relatively high content of organic carbon that usually occurs together with sulfide minerals in the shales has a deleterious influence on the results from several of the well-established procedures used in silicate analysis, invalidating these assumptions. Organic carbon and sulfide mineralization prevent accurate measurement of ferrous iron and H_2O^+ and also affect the relation of H_2O^+, ferrous iron, sulfur, C_{org}, and CO_2 to LOI. However, if the relation of LOI to iron speciation and the volatile components can be well understood, the content of hydrogen bound in organic matter can be calculated for the final summation of the analysis. In this report, the LOI relation to other components is first discussed on a general level, and then the appropriate calculations are applied to data obtained for SDO–1 using common laboratory procedures for silicate rock analysis. All ignition reactions pertinent to the discussion that follows, the errors in LOI and total results that ignition reactions introduce, and appropriate corrections are summarized in table 1.

RELATION OF VOLATILE COMPONENTS TO LOI

Normal Igneous Rocks

In typical silicate rock analysis, LOI approximates the sum in the sample of volatile components, mainly CO_2 expelled from carbonate, S, H_2O^+, and halogens. Therefore, it should be possible to calculate one of the volatile components, H_2O^+, by difference from the rest and the measured LOI (LOI_{exp}). However, some of the sample constituents change during ignition, causing analytical error to be introduced in the estimation of volatile components from LOI_{exp}. Proper corrections must be introduced to obtain a corrected value, LOI_{corr}, which will equal, rather than only approximate, the sum of the volatile components.

The effect on LOI_{exp} of oxidizing ferrous iron is a well-known example. Commonly, in the analysis of igneous rocks, the LOI_{exp} is decreased in comparison to LOI_{corr} by the weight gain from adding oxygen to the sample during

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Table 1. Reactions during ignition and their effect on the relation between LOI and Σ volatile components

	Sample components	Cation stays in ignited residue as	Volatile components as	Correction for LOI_{corr} = Σ volatile components	Notes
1	MCO_3	MO	CO_2		
2	$M_xO_y \times nH_2O$	M_xO_y	H_2O		
3	MX	MO or M_2O	X_2		
4	$MF+nH_2SiO_3$	MO	H_2SiF_6		Uncertain but generally neglibigle.
5	FeO	Fe_2O_3		FeO×0.111	
6	FeS	$Fe_2O_{3\times}$	SO_2	S×0.7484	
7	FeS_2	Fe_2O_3	$SO_2S\times0.3742$		
8	$FeS_2+(Ca,Mg)CO_3$	$Fe_2O_3+a(Ca,Mg)SO_4$	$(4-a)SO_2+CO_2$	$0.3742+S_{ignit}\times1.497$	With SO_2 fixation.
9	$C_xH_yO_zN$		CO_2+H_2O+NO		H_2O^+ determination biased high by oxygen fixed in oxidizing H_{org}.

M=alkali or alkaline earth
X=Cl, Br, I

S_{ignit}=S content in ignited residue
H_{org}=hydrogen in organic matter

Reactions:	Apply to:
1–5	Typical igneous rocks; occasionally reactions 6–7 also apply, but the corrections will be negligibly small
Up to 8	Sulfide-rich rocks, but 5–8 will dominate errors
Up to 9	Organic-rich rock

ignition, oxidizing divalent iron to trivalent. In the absence of sulfur, the correction is rather straightforward and may be expressed as

$$LOI_{corr}=C+CO_2+H_2O^+=LOI_{exp}+FeO\times0.111$$
$$=\Sigma \text{ volatile components.} \qquad (1)$$

The multiplication factor 0.111 is the molecular mass ratio of Fe_2O_3 to 2FeO minus 1, and the product expresses the mass increase of the ignited sample due to fixation of oxygen through oxidation of the originally divalent iron. After making this correction to LOI_{exp}, the calculation of H_2O^+ in "typical" igneous rocks from LOI_{corr} and the other volatile components can be made with considerable accuracy.

Also during ignition,the halogens F and Cl are partially lost from samples. At high ignition temperatures, when H_2O^+ is released, pyrohydrolysis takes place, and Cl volatilizes as HCl. The process is supported by the SiO_2 present, which acts as a nonvolatile acid. Fluorine behaves in a similar way, but the HF formed reacts immediately with SiO_2 and volatilizes as SiF_4 or H_2SiF_6. The losses are greater for acid rocks than for basic ones. In most cases, the error in SiO_2 affecting the final analytical summation is negligible, and inclusion of halogens in the sum of volatile components is sufficient in obtaining a value for LOI_{corr} from which a calculated H_2O^+ can be accurately derived.

It was noted above that FeO, normally measured straightforwardly in "typical" silicate rock analysis, cannot be measured directly in the presence of organic matter. Also ferrous iron in pyrite is not measured using the standard ferrous iron procedure. Obtaining LOI_{corr} for SDO–1, then, is not straightforward; the remainder of this section examines the problem.

The Effect of Sulfidic Sulfur

If sulfur is present in appreciable amount (>0.2 percent), the error in LOI_{exp} becomes more complicated. Most often the sulfur in shales occurs bound to iron either as pyrite/marcasite (FeS_2) or as pyrrhotite (FeS). However, all iron is typically reported as Fe_2O_3 in rock analyses. This misrepresentation of iron speciation in the final summation of oxides results in a positive numerical error since both the sulfur actually bound to iron and the "sulfur equivalent" oxygen (SOQ) reportedly bound to iron are included. The oxide summation is corrected by subtracting SOQ from the initial summation. For pyrite the SOQ is S×0.25 (16/2×32.06), whereas for pyrrhotite it is S×0.5 (16/32.06). Thus, accurate correction requires knowledge of the mode of sulfur occurrence in the sample.

It is possible to differentiate between the pyrite and pyrrhotite by showing differences in the solubilities of the two materials or by using a qualitative test; the presence of pyrrhotite is revealed by the smell of H_2S when adding acid to the sample. A common-sense judgment can also be used, based on the fact that pyrrhotite generally occurs in basic rocks, whereas pyrite and marcasite are common in shales. Further discussion will therefore be limited to considering occurrences of pyrite in the sample.

In addition to the SOQ correction in the major oxide total, a correction of LOI_{exp} must also be introduced for the oxygen mass added to oxidize pyritic (divalent) iron to

Fe_2O_3. This oxygen increases the mass of the ignited sample and reduces LOI_{exp} in comparison to LOI_{corr}, as already discussed for samples containing ferrous oxide. Assuming that the sulfur is bound more or less exclusively to iron, this correction is made by multiplying the sulfur content by 0.3742:

$$LOI_{corr}=S+CO_2+H_2O^+=LOI_{exp}+(S\times 0.3742). \quad (2)$$

However, this correction might be inadequate if the sample contains $CaCO_3$ or $MgCO_3$, either of which can fix S in the ignited sample as sulfate. The direct determination of CO_2 as one of the volatiles in the sample gives an indication of the potential magnitude of this problem. Equation 2 also neglects oxidation of any ferrous iron in addition to pyritic iron. To account for both sulfur fixation and that oxidation, equation 2 becomes

$$LOI_{corr}=(S-S_{ignit})+CO_2+H_2O^+$$
$$=LOI_{exp}+FeO\times 0.111+S\times 0.3742+S_{ignit}\times 1.497. \quad (3)$$

The Effect of Inherent Sulfate Occurrences on LOI

Although the discussion above assumed that essentially all sulfur in the sample occurred as pyrite or pyrrhotite, sulfur may also be present in the sample initially as sulfate. Sulfates of alkali and alkaline earth elements are unaltered during ignition, whereas sulfates of heavy or trivalent metals (for example, Fe, Mn, Cu) decompose, releasing SO_3. Oxidation of sulfide to sulfate is a common natural geochemical process and may even take place during storage of the sample in the laboratory, particularly for samples containing considerable H_2O^- stored at high temperatures.

The presence of alkaline earth sulfates in the sample generally results in an analytical summation low by an amount equal to the excess oxygen in sulfate compared to oxide, $S_{sulf}\times 1.497$. The presence of alkaline earth sulfates, however, does not cause an error in the estimation of H_2O^+ from equations 2 or 3. On the contrary, the presence of heavy metal sulfates would overestimate H_2O^+, using those equations, by the excess of oxygen in sulfate compared to oxide, that is, by $S_{sulf}\times 1.497$.

The Effect of Organic Carbon on LOI

During ignition to determine LOI_{exp}, all organic matter in the sample is oxidized and volatilized:

$$\text{Volatile components}$$
$$=(CHON)_{org}+S+CO_2+H_2O^+_{true}. \quad (4)$$

The ignition should proceed slowly at a temperature that avoids melting of the sample; otherwise, incomplete oxidation of carbon and partial reduction of Fe_2O_3 to FeO might occur in the molten sample. Either would result in a low LOI_{exp}, and an error in the calculation of H_2O^+.

Assuming that complete oxidation of organic matter also occurs during determination of H_2O^+ in organic-rich samples, the measured H_2O^+ will be higher than the amount calculated from LOI and the other individual volatile components (eq. 2). This difference occurs because organic hydrogen will be oxidized to water and included in the measured H_2O^+ result. The excess water can be used to estimate the hydrogen bound in hydrocarbons:

$$H_2O^+{}_{meas}-H_2O^+{}_{calc}=9\times H_{org}. \quad (5)$$

Further, the calculated value can be used to approximate the true constitutional water in the sample, which cannot be as accurately measured in organic-rich samples as in "typical" rocks.

EXPERIMENT PARAMETERS

The SDO–1 sample was analyzed on an "as received" basis, except for LOI_{exp}, which was determined on the dry sample. Duplicate analyses from each of two bottles of SDO–1 were made using methods routinely applied in the authors' laboratory (Weiss, 1983; Huka and Rubeska, in press). The samples were analyzed as part of a batch (~200) of routine samples. The major oxides that are required for the analytical summation were determined from a single decomposition of the sample using a mixture of HF, HNO_3, and H_2SO_4. A 0.200-g sample was decomposed in a specially designed polytetrafluoroethylene vessel assembly where the evolving SiF_4 was sorbed on KNO_3. After hydrolysis of the resulting K_2SiF_6, Si was determined by titrating the released HF with NaOH (Huka and Rubeska, in press). Fluorides in the sample residue were removed by fuming after the addition of H_3BO_3 and HNO_3. About 50 mL of distilled water were added to the dry residue, and the sample was left on a warm plate to hydrolyze for 20 to 30 minutes. Then, 10 mL 1:1 HCl, with 0.2 g Cs_2CO_3 and 0.25 mL H_2SO_4 as an ionization buffer, were added. The resulting clear solution was transferred to a 100-mL volumetric flask and made up to volume with distilled water. Li, Na, K, Mg, Ca, Ti, and Mn were measured by flame atomic absorption spectrometry (Fl–AAS). Fe_{tot} and P_2O_5 were determined by spectrophotometry, using the sulfosalicylic acid and molybdenum blue procedures, respectively. Al was determined by the Sajo (Weiss, 1983) chelatometric method with ethylenediamine tetraacetic acid.

Moisture (H_2O^-) was determined to be 0.79 weight percent by drying the weighed sample at 110°C for 4 hours and reweighing. LOI was determined on the dry sample,

Table 2. Results of major rock-forming constituent analyses of SDO–1

[In weight percent]

Split: Component	393a	393b	768a	768b
SiO_2	49.43	49.29	49.62	49.26
Al_2O_3	12.06	12.13	12.10	12.03
Fe_2O_3	3.03	2.98	3.04	3.07
FeO	5.64	5.66	5.59	5.63
MnO	.041	.040	.040	.042
MgO	1.47	1.46	1.48	1.49
CaO	1.01	1.07	1.08	1.06
Li_2O	.006	.006	.006	.006
Na_2O	.45	.43	.43	.42
K_2O	3.24	3.23	3.23	3.22
P_2O_5	.01	.01	.01	.01

Table 3. Volatile components as measured in SDO–1

[In weight percent]

Split: Component	393a	393b	768a	768b
F	<0.01	<0.01	<0.01	<0.01
C_{tot}	10.41	10.40	10.48	10.57
CO_2	.72	.70	.81	.84
$C_{org}=C_{tot}-C_{CO^2}$	10.21	10.21	10.26	10.35
S	5.04	5.05	4.99	5.03
$H_2O^+_{meas}$	9.66	9.46	9.53	9.28
Volatile components	25.63	25.42	25.59	25.49
LOI_{exp}	21.59	21.45	21.56	21.51

which was ignited at 1,050°C for 20 minutes and reweighed. Carbonate was measured by the release of CO_2 from the sample by boiling with H_3PO_4 and its sorption on $Ba(OH)_2$; the sorbed CO_2 was titrated using a Stroehlein Coulomat Model 7012. Total carbon was determined from the CO_2 released by igniting the sample in a stream of oxygen, measured as just described for CO_2 in the sample. Sulfur was determined after its release as SO_3 by heating the sample with a catalyst, $V_2O_5+U_3O_8$, in a stream of nitrogen. After sorption, the SO_3 was titrated with coulometrically generated iodine, using biamperometric indication of the endpoint.

Rare earth analyses were performed by inductively coupled plasma atomic emission spectrometry following two different procedures for the separation of the rare earth elements (REE) from the sample matrix. One using ion-exchange chromatography was described by Sulcek and others (1989); the second involved an organic solvent extraction of ion associates of REE nitrates with trioctylphosphine oxide (Weiss and others, 1990).

RESULTS AND DISCUSSION

Results for major-oxide analyses of SDO–1 are presented in table 2. Results for the volatile components that were measured directly are presented in table 3. Using the logic of the preceding section describing the potential analytical errors in analytical summation and LOI (summarized in table 1), corrections for those errors were made, as follows.

Since it was not possible to determine FeO directly in the presence of organic matter, the assumption was made that all S present occurred in pyrite and that a corresponding stoichiometric amount of Fe^{+2} occurred in the sample. The balance of the total iron was assumed to be ferric iron. Little carbonate was measured in SDO–1; thus, no appreciable amount of S is expected to be fixed in the ignited residue as sulfate. LOI_{corr} from equation 3 is therefore reduced to

$$LOI_{corr}=LOI_{exp}+S\times 0.3742, \qquad (6)$$

which accounts for oxidation of pyrite to hematite.

From this calculated LOI_{corr}, values for volatile components, H_{org}, and true H_2O^+ are derived. Table 4 summarizes these calculations and presents the analytical summation for the analyses, based on those calculations and the major-oxide analyses presented in table 2. The totals are not ideal, due to the uncertainties involved in the approach. However, as can be seen, the approach improves the uncorrected totals significantly.

The REE data by ICP–AES following the two separations are presented in table 5. They agree well with recommended concentrations (Kane and others, 1990) that were derived from these and other contributed data. However, the extraction procedure apparently provides higher results than those obtained using the ion-exchange procedure. This difference probably occurs because, for the extraction, calibration solutions were carried through the separation; whereas for ion exchange, they were not. An ion- exchange yield of less than 100 percent would cause a low bias in the sample analyses. No such bias would occur if extraction yields were less than 100 percent, but constant for sample and calibration solutions.

CONCLUSION

The results presented in this paper formed a part of the compiled data base from which the recommended concentrations were derived for the gas shale reference sample SDO–1. The methods used in our laboratory produce analytical results in excellent agreement with the final recommended concentrations for both major oxides and rare earth elements. Applying the described corrections to LOI provides acceptable major-oxide summations for the analysis of organic-rich and sulfur-rich samples, which are generally quite difficult to achieve for such samples.

Table 4. Calculations for correction of measured volatile components to account for ignition reactions

Calculation	Result in weight percent	Comment
$SOQ=(S)(0.25)$	−1.26	Oxygen equivalent of sulfur for pyritic iron represented as FeO in major oxide table 1; see text E2.
$LOI_{corr}=LOI_{exp}+(S)(0.3742)$	23.43	Oxygen added in oxidizing pyrite to Fe_2O_3; see eq. 2.
$LOI_{corr}=S+C_{org}+CO_2+H_2O^+_{meas}$	25.54	Alternative calculation to that above; see eq. 3.
excess O=eq. 3 LOI_{corr}−eq. 2 LOI_{corr}	2.11	Fixed on oxidation of organic H; see text E3.
H_{org}=excess O÷8	.27	H_2O graumetric factor.
excess H_2O^+=excess O+H_{org}	2.38	
$H_2O^+_{true}=H_2O^+_{meas}$−excess H_2O^+	7.12	See text E3.
Major oxide summation	76.29	Table 1, average
CO_2, C_{org}, S summation	16.06	Unbiased measured volatiles, table 2.
H_2O^-	.79	Moisture; see text E3.
$H_2O^+_{true}$	7.12	Calculated above.
H_{org}	.27	Calculated above.
SOQ	−1.26	Calculated above.
Analytical summation, whole rock	100.53	Meets 100±1 test for overall analytical accuracy.

Table 5. Results for rare earth elements in SDO–1

[In µg/g; NA, not analyzed]

	Ion exchange		Extraction	
Split: Element	393	768	393	768
La	35.3	34.7	38.6	37.3
Ce	71.6	70.9	86.1	84.1
Pr	8.00	7.79	8.55	8.75
Nd	35.3	36.0	35.5	35.9
Sm	7.71	7.36	8.47	7.91
Eu	1.46	1.48	1.65	1.69
Gd	7.06	7.11	8.40	7.80
Tb	.81	1.04	.91	1.01
Dy	6.22	6.33	7.14	7.08
Ho	1.22	1.10	1.31	1.46
Er	3.83	3.00	4.00	3.96
Tm	.49	.50	<.40	<.40
Yb	3.05	3.11	3.80	3.80
Lu	.49	.49	.55	.55
Y	34.8	35.0	40.6	40.2
Sc	13.0	12.5	NA	NA

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Chapter F

A Study to Determine Sources of Interlaboratory Variability in Measured Loss on Ignition (LOI) for Devonian Ohio Shale SDO–1

By JEAN S. KANE and CAROL J. SKEEN

U.S. GEOLOGICAL SURVEY BULLETIN 2046

THE USGS REFERENCE SAMPLE DEVONIAN OHIO SHALE SDO–1

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A Study to Determine Sources of Interlaboratory Variability in Measured Loss on Ignition (LOI) for Devonian Ohio Shale SDO–1

By Jean S. Kane *and* Carol J. Skeen

Abstract

Studies are reported that investigate the several components in the sizable (approximately 10 percent relative) variance between laboratories in measuring loss on ignition for the reference sample Devonian Ohio Shale SDO–1. This large variance is a major factor in the poor analytical summation for the major constituents of the shale that was noted in the original compilation report (Kane and others, 1990).

INTRODUCTION

In reporting recommended concentrations for constituents in the reference shale sample SDO–1, difficulty was encountered in verifying the overall SDO–1 analyses using a major-oxide summation to 100±1 percent (Kane and others, 1990). Such verification is very common in rock analysis (Abbey, 1983; Lechler and Desilets, 1987), but it is less applicable to the analysis of either organic-rich or sulfur-rich samples. For example, totals of the recommended major-oxide concentrations (including estimated volatile components) for marine mud (MAG–1), Cody Shale (SCo–1), and Green River Shale (SGR–1) reference samples are 105.5, 100.35, and 88.82 percent, respectively (Gladney and Roelandts, 1988).

The difficulty results from the inability to measure individual volatile components accurately and from the considerable error that results from using measured loss on ignition (LOI) as a measure of the sum of volatile components (Lechler and Desilets, 1987; Potts, 1987; Huka and Rubeska, chap. E, this vol.). The important volatile components are water (both moisture, H_2O^-, and essential water, H_2O^+), carbon dioxide (CO_2), sulfur (S), and organic matter. Only H_2O^-, CO_2, and S can be measured directly.

In most rock analyses, total water (H_2O_{tot}) and moisture (H_2O^-) are measured, whereas essential, or bound, water (H_2O^+) is calculated by difference. For organic-rich samples, H_2O_{tot} as measured includes both the H_2O^+ in sample and the water resulting from combustion of organic matter. H_2O^+ calculated in the normal way is biased high by the organic matter contribution to H_2O^+.

Although total carbon (C_{tot}) and CO_2 can be measured readily, C_{org} is most often determined by difference between C_{tot} and $C_{carbonate}$ ($CO_2 \times 0.274$). From C_{org}, total organic matter can be estimated, but uncertainties are considerable. Ratios of C to H in organic matter (as determined by CHN analysis of organic matter isolated from shale by Soxlet extraction) are biased low, overestimating H_{org} (Frost and others, 1985). This error occurs because low-molecular-weight organic compounds are preferentially extracted. Correction of H_2O_{tot} for the H_{org} contribution will be correspondingly inexact.

Frost and others (1985) achieved totals generally between 98 and 101 percent, but occasionally as low as 96 percent or as high as 103 percent, for the analyses of a large number (~250) of Devonian shales from Illinois. They assumed that H_2O^+ could be fairly accurately estimated from a hydrogen mass balance after measuring H_{tot} and moisture and calculating an organic hydrogen value. Huka and Rubeska (chap. E, this vol.) present another approach to achieving an accurate analytical summation by estimating H_2O^+ from the experimental loss on ignition (LOI_{exp}). They outline corrections to LOI_{exp} that are required for LOI to approximate more accurately the sum of volatile components in sample. This paper reviews the compiled data relevant to LOI and presents the experiments undertaken in our laboratory to better understand the various components of uncertainty in LOI.

REVIEW OF COMPILED DATA FOR FEO AND VOLATILE COMPONENTS

Table 1 includes all previously contributed and newly reported data for LOI, ferrous iron, and individual volatile components, and for moisture, H, and N. The moisture, H,

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Table 1. Compiled data for volatile components

Moisture (weight percent)		
Data	Lab ID	Method and comment
0.50	Lab 15	
.71	Lab 55	110°C for 1 hr
.73	Lab 31	
.80	Lab 14	110°C for 4 hr
.99	Lab 6	
1.06	Lab 16	
1.58	Lab 17	
1.68	Lab 22	110°C for 18 hr
1.73	Lab 2	
1.79	Lab 3	
1.80±0.29	This work	110°C 1 hr or 18 hr

Constitutional water (weight percent)		
Data	Lab ID	Method and comment
2.93	Compilation Average	Calculated (See Kane and others, 1990)
4.41	17	Unknown
7.12	14	Calculated (See Huka and Rubeska, chap. E, this vol.)

Hydrogen (weight percent)	
Data	Lab ID
1.24	Lab 39
1.30	Lab 30
1.30	Lab 38
1.33	Lab 23
1.34	Lab 32
1.34	This work
1.35	Lab 34
1.40	Lab 29
1.45	Lab 55
1.83	lab 31

Nitrogen (weight percent)	
Data	Lab ID
0.31	Lab 31
.31	Lab 38
.32	Lab 34
.33	This work
.34	Lab 32
.40	Lab 23
.40	Lab 30
1.21	Lab 39

Total carbon (weight percent)		
Data	Lab ID	Method and comment
8.97	Lab 20	
9.27	Lab 27	
9.72±0.72	This work	
9.85	Lab 7	
9.96	Lab 6	
9.96	Lab 19	
9.96	Lab 13	
9.98	Lab 8	
10.00	Lab 28	
10.09	Lab 17	Sum $C_{org}+CO_2$
10.26	Lab 14	
10.36	Lab 23	1,800°C, combustion
10.40	Lab 29	
10.40	Lab 30	
10.40	Lab 34	
10.43	Lab 32	
10.53	Lab 55	Combustion
10.80	Lab 23	Wet oxidation
10.89	Lab 38	
11.80	Lab 39	
13.79	Lab 31	

Carbonate C as CO_2 (weight percent)		
Data	Lab ID	Method and comment
0.45	Lab 13	
.55	Lab 57	
.75	Lab 4	
.77	Lab 14	
.63–0.81	This work	Assuming measured C in residue of 500°C ash approximates carbonate C
.85	Lab 15	
.99	Lab 28	
.99	Lab 29	
1.07	Lab 1	
1.08	Lab 27	
1.25	Lab 37	
1.28	Lab 19	
1.46	Lab 3	

Organic C (weight percent)		
Data	Lab ID	Method and comment
8.30	Lab 20	Unspecified
8.79	Lab 20	Calculated by difference (total-carbonate)
8.98	Lab 28	Leco
9.72	Lab 17	Unspecified
9.73	Lab 13	Calculated
10.08	Lab 23	Calculated
10.11	Lab 38	Unspecified
10.19	Lab 55	Calculated
10.20	Lab 7	Unspecified
10.44	Lab 23	Wet oxidation
10.52	Lab 8	Unspecified
11.30	Lab 39	Unspecified

Sulfur (weight percent)		
Data	Lab ID	Method and comment
Sample as received		
4.90	Lab 29	
5.03	Lab 14	
5.06	Lab 19	
5.19	Lab 13	
5.23	Lab 15	
5.29	Lab 58	
5.30	Lab 28	
5.36	Lab 27	
5.38	This work	Leco
5.70	Lab 57	
6.30	Lab 20	

Table 1. Compiled data for volatile components—Continued

Sulfur (weight percent)—Continued		
Data	Lab ID	Method and comment
Ignited sample		
0.71	Lab 21	XRF
.43	This work	Leco, 1,000°C
1.41	This work	Leco, 500°C

Loss on ignition (weight percent)		
Data	Lab ID	Method and comment
19.25	This work	500°C, 1 hr
19.43	This work	500°C, 18 hr
19.56	Lab 3	
19.56	Lab 1	550°C, 1 hr
19.78	Lab 27	
20.82	This work	800°C, 1 hr
20.83	Lab 13	
20.91	Lab 18	
21.37	Lab 58	
21.38	Lab 16	
21.57	Lab 6	
21.63	Lab 4	1,000°C, 1 hr
21.82	Lab 17	
21.90	Lab 21	
21.93	Lab 15	
22.00	Lab 57	
22.35	Lab 26	
22.37	Lab 19	
22.39	Lab 14	1,050°C, 20 min
22.84	Lab 2	
23.06	This work	1,000°C, 1 hr
23.08	Lab 22	1,000°C, 1 hr
33.00	Lab 20	

and N data were not included in the 1990 compilation (Kane and others).

An examination of the compiled data reveals four points. First is the general lack of data for individual volatile components in comparison to major oxides, each of which was reported by 20 to 30 contributors. Second is that LOI, CO_2, and H_2O^- all show an unacceptably large variation between laboratories. For LOI, fewer than half the contributing laboratories reported ignition temperature, which significantly affects experimental LOI. For example, the omission of the obvious outlier value of 33-percent LOI results in the 3.5-percent absolute difference between the high and low laboratory average LOI. This variation results from several factors, one of which is the significant between-bottle variation for LOI noted in the 1990 compilation (Kane and others). Five of eight laboratories identified between-bottle variance, which may be equally significant for H_2O^- and CO_2, although the data reported does not permit assessment of that possibility.

Variation of ignition temperature is the third factor contributing to between-laboratory variance. Laboratories reported using various ignition temperatures from 500°C to 1,000°C. Although ignition to constant weight occurs within 1 hour at 1,000°C (Lechler and Desilets, 1987), it proceeds more slowly at lower temperatures. Therefore ignition at 500°C for one hour is incomplete and the LOI result is biased low. This factor will be treated more fully in the results and discussion section.

Also, few laboratories indicated whether or not samples were ignited "as received" or after drying. If H_2O^- was not reported separately, LOI was assumed to have been reported on an "as received" basis so that the final recommended LOI result includes H_2O^- along with all other volatile components. Similarly, if H_2O^- was reported separately, it was assumed that the reported LOI did not include moisture and that value was added, so that LOI as compiled would include it. If either (or both) of these assumptions is incorrect, that would account for a part of the observed between-laboratory variance in LOI results.

The final point to note regarding the compiled data in table 1 is that LOI as measured does not accurately reflect the sum of volatile components (Lechler and Desilets, 1987; Huka and Rubeska, chap. E, this vol.; Potts, 1987). Therefore, LOI cannot be used with the major rock-forming oxides in achieving an accurate analytical summation. For typical rock analysis, the inaccuracy is due almost exclusively to the weight gain resulting from oxidation of ferrous oxide to ferric oxide (Lechler and Desilets, 1987). Since FeO and total iron can both be measured directly and accurately for most rocks, correction is straightforward. For sulfur-rich and organic-rich sedimentary rocks (and SDO–1 is both), the error is of similar origin—oxidation of both pyritic iron and ferrous oxide to ferric oxide. Correction for this error is complicated in two ways. First is the inability to measure ferrous iron directly in the original sample due to interferences in the redox reactions for that measurement by both organic matter and sulfur. Second is an additional error in measured LOI due to the weight gain resulting from fixation of some sulfur as sulfate in the ignited sample. Correction for that error requires measurement of sulfur in the ignited sample; only one laboratory initially reported that measurement.

This study focused on establishing the significance of between-bottle differences for H_2O^-, CO_2, and organic matter in sample and on the degree of ferrous iron oxidation and sulfur fixation during ignition.

EXPERIMENT PARAMETERS

Moisture (H_2O^-) and LOI

Both H_2O^- and LOI were measured following the standard procedures of the laboratory (Jackson and others, 1987; Shapiro and Brannock, 1962), which involve overnight drying at 105°C and 1-hour ignition at 1,000°C. The H_2O^- and LOI contents were determined in duplicate for four separate bottles to allow between-bottle analysis of variance (anova) calculations. The constituent concentrations were obtained as the differences in weight between "as received" and dried/ignited sample weights.

Reabsorption of moisture by dried or ignited samples was measured as follows. Accurately weighed, dried/ignited samples, one from each bottle of SDO–1, were stored in separate sealed vials. The second samples from each bottle were left exposed to a humid (>90 percent) laboratory atmosphere in open vials. Both groups were reweighed 8 hours later, and the reabsorbed moisture was calculated by difference. The dried (but not ignited) samples were returned to the drying oven after reabsorption, and the process was repeated through three cycles.

In addition to the standard ignition for 1 hour at 1,000°C, three other time/temperature ignitions were done to assess variations in results attributable to drying time and temperature: 1 hour at 500°C; 18 hours at 500°C, and 1 hour at 800°C. LOI was generally determined on the "as received" sample; in some cases LOI was determined on the dried sample instead.

Determination of Ferrous Iron

For the ignited samples only, FeO was measured by titration with potassium dichromate to a diphenylamine sulfonate indicator endpoint using the procedure reported in Shapiro and Brannock (1962). The ash was first decomposed in the absence of air with a mixture of hydrofluoric and sulfuric acids.

Table 2. Moisture: Evaluation of bottle differences
[In weight percent; d.f., degrees of freedom]

Bottle	Result—overnight drying	F–test data
1	1.57±0.023	d.f.=7,13
6	1.64±0.015	F=50.40
5	1.69±0.025	
4	1.73±0.03	
2	2.02±0.14	$F_{crit}(0.95)=2.83$
7	2.04±0.021	$F_{crit}(0.99)=4.44$
3	2.22±0.098	
Average, individual results, all bottles	1.84±0.29	
Bottle	**Result—1-hr drying**	
1	1.59	
4	1.70	
5	1.71	
6	1.62	

Measurement of CHNS

Carbon, hydrogen, and nitrogen were measured in replicate samples from three bottles of SDO–1 using a Perkin Elmer Model 2400 CHN Elemental Analyzer; and S was measured using a Leco Model SC–132 sulfur analyzer on both "as received" and ignited samples. Measurements are based on combustion to convert the elements in sample to simple gases (C to CO_2, H to H_2O, N to N_2, and S to SO_2). CHN are measured by thermal conductivity after chromatographic separation, and S is measured by an infrared detector (Leco, 1980, Perkin Elmer, 1988). These data allow estimation of homogeneity with respect to individual C, H, N, and S samples, which had not been possible before.

RESULTS AND DISCUSSION

Moisture (H_2O^-)

We have noted that several laboratories included moisture in their LOI values, since they ignited samples "as received." Subtle changes in the degree to which samples exhibit hygroscopic behavior and absorb atmospheric moisture are perhaps related to the between-bottle variation in the ratio of clay minerals to other principal components, namely pyrite and organic matter. Such between-bottle variation is evident from the inhomogeneity found with respect to SiO_2, Al_2O_3, and total iron reported as Fe_2O_3, which has been documented (Kane and others, 1990).

H_2O^- measured in this work varied significantly between bottles, as shown in table 2. Overnight drying was used in this study; some laboratories (for example, Frost and others, 1985) employed much briefer drying times of 1 hour. Presumably, this short time was intended to avoid the potential loss of volatile organic compounds from the sample (Jackson and others, 1987). Our results are among the highest moisture contents of the data contributed to the SDO–1 characterization, suggesting a high bias due to loss of organic matter during drying. However, a considerable fraction of the lost weight was restored as reabsorbed moisture in rather short (8-hour) intervals, and more than 85 percent of the lost weight was restored in a 3-day exposure to moist air (fig. 1). Also, moisture determined subsequently in our laboratory using a drying time of 1 hour gave the same moisture results as 18-hour drying had given. Differences in moisture content from bottle to bottle seem to be the principal source of between–laboratory variance in the moisture determination and, therefore, also a principal factor in the reported between–laboratory variance for LOI.

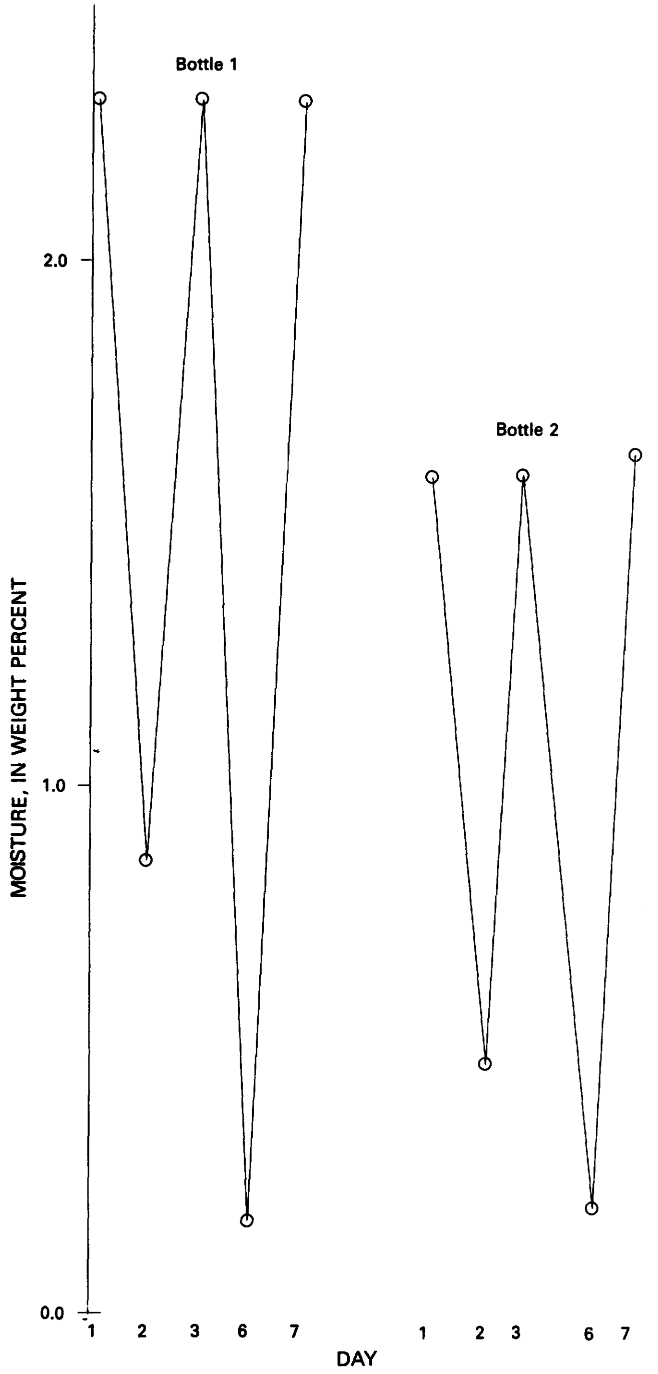

Figure 1. Moisture results after cyclic drying and reabsorption. Days 1, 3, 7: after overnight drying; day 2: after 8 hours exposure to moist air; and day 6: after 3 days exposure to moist air.

LOI

In this study, as well as in the original compiled data, LOI measured both on an "as received" basis and on a dry basis showed considerable variation between bottles (table 3). This variation suggests that organic matter, as well as clay, pyrite, and moisture, are heterogeneously distributed between bottles. The compiled total carbon, organic carbon, and CO_2 results in table 1 do not allow adequate homogeneity evaluations, as reported. Bottle–to–bottle moisture variation, discussed above, accounts for approximately half the observed LOI between–bottle variance; between–bottle variation of organic matter could account for most of the remaining variance. CHN data from this study appear to confirm this theory.

Weight gain from pyritic and ferrous iron oxidation and possibly from sulfur fixation also accounts for some of the observed between–bottle variance in LOI. These aspects of between–bottle and between–laboratory variance in LOI will be discussed in the next two sections.

The reactions that potentially occur during ignition are summarized in table 4. All are well–documented through differential thermal analysis (DTA) studies (Liptay, 1971; Warne, 1979) to be dependent on ignition temperature. These studies indicate that CO_2 will not be lost from calcite below 800°C; however, magnesite and siderite lose CO_2 at 580 to 690°C and 540 to 620°C, respectively. Similarly, pyrite oxidizes to hematite with release of SO_3 in the neighborhood of 580°C. Because DTA studies are carried out under very different ignition conditions from those for determination of LOI, the reaction temperatures found through DTA experiments do not duplicate those for ignition reactions; however, DTA results do indicate potential sources of variation in LOI with ignition temperature. These factors collectively could explain the observed between–laboratory variation that cannot be attributed to between–bottle moisture and (or) organic–matter variations.

One–way anova with temperature as the classification variable (table 3) shows the significance of temperature variation. Two–way anova shows the interaction between temperature and bottle as a source of variation. That interaction is reflected in the nonparallel plots of LOI vs ignition temperature for the several bottles included in this study (fig. 2). This interaction implies that each of the contributions of each of the reactions in table 4 to the measured LOI varies somewhat bottle to bottle.

FeO and S in Ignited Sample

Total iron reported as Fe_2O_3 is 9.36±0.22 percent in SDO–1; however, based on geochemical and petrological evidence (Leventhal and Hosterman, 1982, Frost and others, 1985), little or none of the iron present occurs as ferric iron. All iron is instead thought to occur either in pyrite or as ferrous iron, occurring mainly in clays, oxides, and to a lesser extent in carbonates. Experimentally, both FeO and S were determined in samples after ignition. Results of those measurements are given in table 5.

The data show essentially complete oxidation of ferrous oxide/carbonate and pyrite at all three ignition

Table 3. Loss on ignition (in weight percent): Evaluation of bottle and ignition-temperature differences

[LOI, loss on ignition; d.f., degrees of freedom; leaders (—), no data]

	Results for LOI as received			
Bottle	550°C, 1 hr	550°C, 18 hr	800°C, 1 hr	1,000°C, 1 hr
1	19.49	19.43	20.89	22.69
2	19.97	—	21.88	23.22
3	19.95	—	22.19	23.73
4	19.40	20.01	21.04	22.61
5	—	—	—	23.72
6	—	—	—	21.58
7	19.49	—	—	23.05
8	18.65	18.85	20.15	21.58
Average	19.25±0.54	19.43±0.53	20.82±0.86	23.03±0.59
F–test data:				
d.f.	2,6		3,4	4,9
F	13.3		115.6	80.44
Probability LOI same, all bottles	0.007		0.001	<0.001
F_{crit} (0.95)	5.14			6.59

Table 4. Reactions during ignition of sample

Reaction	Reaction temperatures for specific minerals (Liptay, 1971; Warne, 1979)	
$MCO_3 \rightarrow MO + CO_2\uparrow$	Siderite:	540–620°C
	Magnesite:	580–690°C
	Calcite:	>800°C
$FeS_2 \rightarrow Fe_2O_3 + SO_2\uparrow$	Begins at:	580°C
	Complete reaction:	>1,000°C
Hydrous clays→anhydrous+$H_2O\uparrow$	Illite:	500–550°C
	Kaolinite:	550–620°C
	Montmorillonite:	700–730°C
Organic matter→CO_2+H_2O	Essentially complete	≥1500°C

temperatures (500°C, 800°C, and 1,000°C). This result contrasts with the Lechler and Desilets (1987) report that oxidation is complete only at 100°C ignition. The weight gain of sample during ignition due to iron oxidation, therefore, should be the same regardless of ignition temperature. Assuming that all iron in SDO–1 is ferrous initially, and that it is totally oxidized to hematite (Fe_2O_3), that gain amounts to 2.25 percent, as shown in table 5.

Our data also indicate extensive sulfur retention (>20 percent of initial S) at 500°C ignition, which decreases to approximately 10–percent retention at 1,000°C ignition. Based on the data in table 5, the weight gain of sample will be maximum, approximately 2 percent, for ignition at 500°C, 1.5 percent for ignition at 800°C, and 0.75 percent for ignition at 1,000°C. The calculation is given in table 5.

CHN in Both "As Received" and Ignited Sample

Comparison of data for C and H in "as received" and ignited sample indicates both complete oxidation of all organic matter and nearly complete removal of constitutional water at 500°C. Bottle differences exist for C at both the 95–percent and 99–percent confidence levels but are less conclusive for H, existing only at the 99–percent confidence level (table 6). The data also appear to indicate that carbonate remains in 500°C ash but is totally expelled as CO_2 in 800°C ash.

ANALYTICAL TOTAL

LOI as measured was shown above to be low by 2.71 percent (1,000°C) to 4.47 percent (500°C), based on weight

Table 5. FeO and S in ignited sample residue and weight gain calculations (in weight percent)
[d.f., degrees of freedom; leaders (—), no data]

Analytical data

	As received	After ignition at					
		500°C		800°C		1,000°C	
Bottle	S	S	FeO	S	FeO	S	FeO
1	5.50±0.07	1.40	0.16	0.95	0.08	0.44	0.08
2	5.38±0.03	1.41	.12	.97	—	.46	.06
3	5.28±0.05	1.60	—	1.00	—	.44	—
Average	5.38±0.11						
F–test data:							
d.f.	2,6						
F	248						
Probability S same, all bottles	<.001						
F_{crit} (0.95)	5.14						

Weight gain calculations

Oxidation of iron

Reaction	Starting weight percent ×	Gravimetric factor =	Final weight percent	Gain in weight percent
Pyritic $Fe^{+2} \rightarrow FeO$	4.66	$\frac{55.85+16}{55.85}$	5.99	1.33
FeO (from pyrite)$\rightarrow Fe_2O_3$	5.99	$\frac{2(55.85)+3(16)}{2(55.85+16)}$	6.65	.66
2FeO (from clays, etc.)$\rightarrow Fe_2O_3$	2.41		2.67	.26
Total gain				2.25

Fixation of sulfur

Reaction	Comment	Gravimetric factor	Gain in weight percent
$XO+S=+1\frac{1}{2}O_2XSO_4$	Three oxygens for every sulfur fixed, or where X=Mg, Ca, Fe	$\frac{3(16)}{32}*S_{fix}$	$1.5*S_{fix}$
	At 550°C ignition	(1.5) (1.4)	=2.1
	800°C	(1.5) (1.0)	=1.5
	1000°C	(1.5) (0.45)	=0.68

Table 6. CHN results for SDO–1
[In weight percent; d.f., degree of freedom]

	As received			After ignition					
				at 500°C			at 800°C		
Bottle	C	H	N	C	H	N	C	H	N
1	9.92	1.23	0.31	0.22	0.04	0.06	<0.01	<0.01	0.05
2	9.66	1.38	.33	.17	.04	.04	<.01	<.01	.06
3	9.59	1.41	.35	.18	.05	.07	<.01	<.01	.06
Average	9.72	1.34	.33	.187	.043	.057	<.01	<.01	.057
CO_2 equivalent				0.63–0.81			<0.03		
F–test data:									
d.f.	2,6								
F	248	5.92	2.66						
Probability bottles same	<.001	.038	.15						

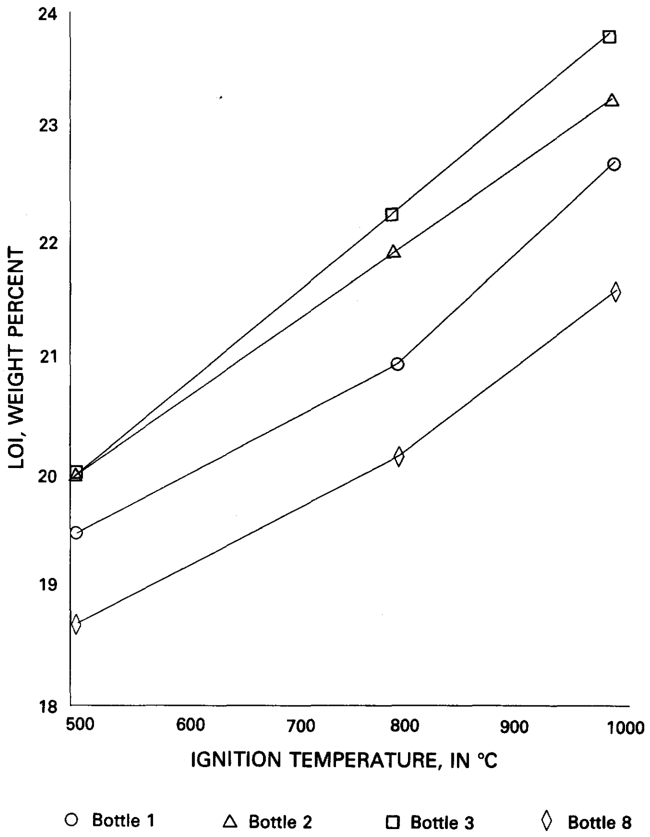

Figure 2. LOI as a function of temperature, illustrating interaction between temperature and bottle components of variance.

Table 7. Alternative estimates of the sum of volatile components

[Leaders (—), no data]

	Volatile components as corrected		
	500°C	800°C	1,000°C
LOI	19.25	20.83	23.06
SO_3 in ash	1.40	1.0	.45
Gain from Fe oxidation	2.26	2.26	2.26
CO_2 residue	1.01	—	—
Total volatile components	23.92	24.09	25.77
Total oxides*	75.81	75.81	75.81
Analytical summation	99.73	99.90	101.58
	Estimate of individual volatiles from compilation averages		
Organic=C_{org}×1.3	12.57		
CO_2	1.01		
H_2O^+	2.63		
H_2O^-	1.60		
S	5.35		
Total volatile compoments	23.16		
Total oxides*	75.81		
Analytical summation	98.97		

*Summation includes pyritic iron as Fe^{+2}, balance of total iron as FeO, in weight percent.

gains during ignition due to iron oxidation and sulfur fixation that varied as a function of ignition temperature and on failure to expel CO_2 at 500°C. The sum of volatile components, based on correction of measured LOI, should therefore be 23.92–25.77 percent. The original analytical summation of recommended concentrations for (nonvolatile) major rock–forming oxides was calculated having iron appropriately included as Fe^{+2} from pyrite or FeO. That summation is 75.81 percent without the volatile components, and 99.73 percent to 101.58 percent including volatile components, based on LOI corrections for 500°C and 1,000°C ignition (table 7). Alternatively, the sum of volatile components can be estimated to be 23.16 percent, as shown in table 7, leading to a final summation of 98.97 percent.

CONCLUSION

With proper understanding of the components in measured LOI, accurate totals of 100±2 percent can be achieved for sulfur– and (or) organic–rich samples, of which SDO–1 is representative. The acceptability of the totals does not ensure that the individual recommended concentrations are correct but nonetheless adds to our confidence in those concentrations.

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Chapter G

Analysis of SDO–1 Pressed Powder Pellets by X-ray Fluorescence—A Note of Caution

By OTTO C. KOPP and FRANCIS C. FURMAN

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THE USGS REFERENCE SAMPLE DEVONIAN OHIO SHALE SDO–1

Analysis of SDO–1 Pressed Powder Pellets by X-ray Fluorescence—A Note of Caution

By Otto C. Kopp *and* Francis C. Furman[1]

SDO–1 is an organic-rich shale relatively high in sulfur. Caution should be used in analyzing this shale by X-ray fluorescence (XRF) using a pressed-pellet technique, such as described by Wheeler (1984). Most available standards, used to generate the calibration curves and to establish corrections for any matrix effects encountered in the analysis, contain lower concentrations of sulfur and organic matter than SDO–1 and, therefore, have matrix characteristics quite different from SDO–1.

We attempted to analyze SDO–1 using our standard procedures. Representative splits were air-dried at 105°C for 1 hour and ground in a swing mill ("shatterbox") for 6 minutes; the pellets were pressed at 30,000 psi for 1 minute. The concentrations for most elements did not agree with the recommended values for SDO–1 (Kane and others, 1990). After considering several sources of error, we concluded that our results were rendered invalid primarily by the high concentrations of organic matter and sulfur in SDO–1. Our analytical protocol is based on standard reference materials that are low in organic matter and sulfur. The maximum organic carbon concentration in our standards is unknown while the maximum sulfur concentraztion is 1.89 percent. These concentrations are 9.6 percent C_{org} and 5.35 percent S in SDO–1.

Perhaps we had become complacent because our analytical protocol for clays, shales, and soils had performed so well over a period of several years. Only when the interelement correction steps were reexamined did we realize the magnitude of the errors that could be introduced. Although the use of elements such as sulfur to make interelement corrections for major elements may seem unusual, the presence of sulfur reflects matrix effects that can enhance (or absorb) some of the secondary X-rays generated for other elements.

Hence, a word of caution is advisable to all who use pressed pellets to perform XRF analyses of atypical samples such as SDO–1. Results are questionable if the net intensities or calculated concentrations for any elements, and especially those elements used in the matrix correction steps, fall outside the ranges of the standards used in generating the protocol. Information about the reference standards and interelement correction steps, possibly unknown to most users, can be critical to analytical accuracy.

Matrix effects can be reduced by analyzing samples fused with a flux such as lithium tetraborate (for example, Spies and others, chap. B, this vol.). However, the fusion technique is more time-consuming and costly than preparing pellets; and the addition of a flux reduces the concentrations of trace elements that might be determined simultaneously, making their determination less precise or even diluting them to concentrations below their detection limits.

The problem will ultimately be resolved when new standards with high sulfur concentrations and organic-rich matrices (such as SDO–1) are added to the analytical protocol.

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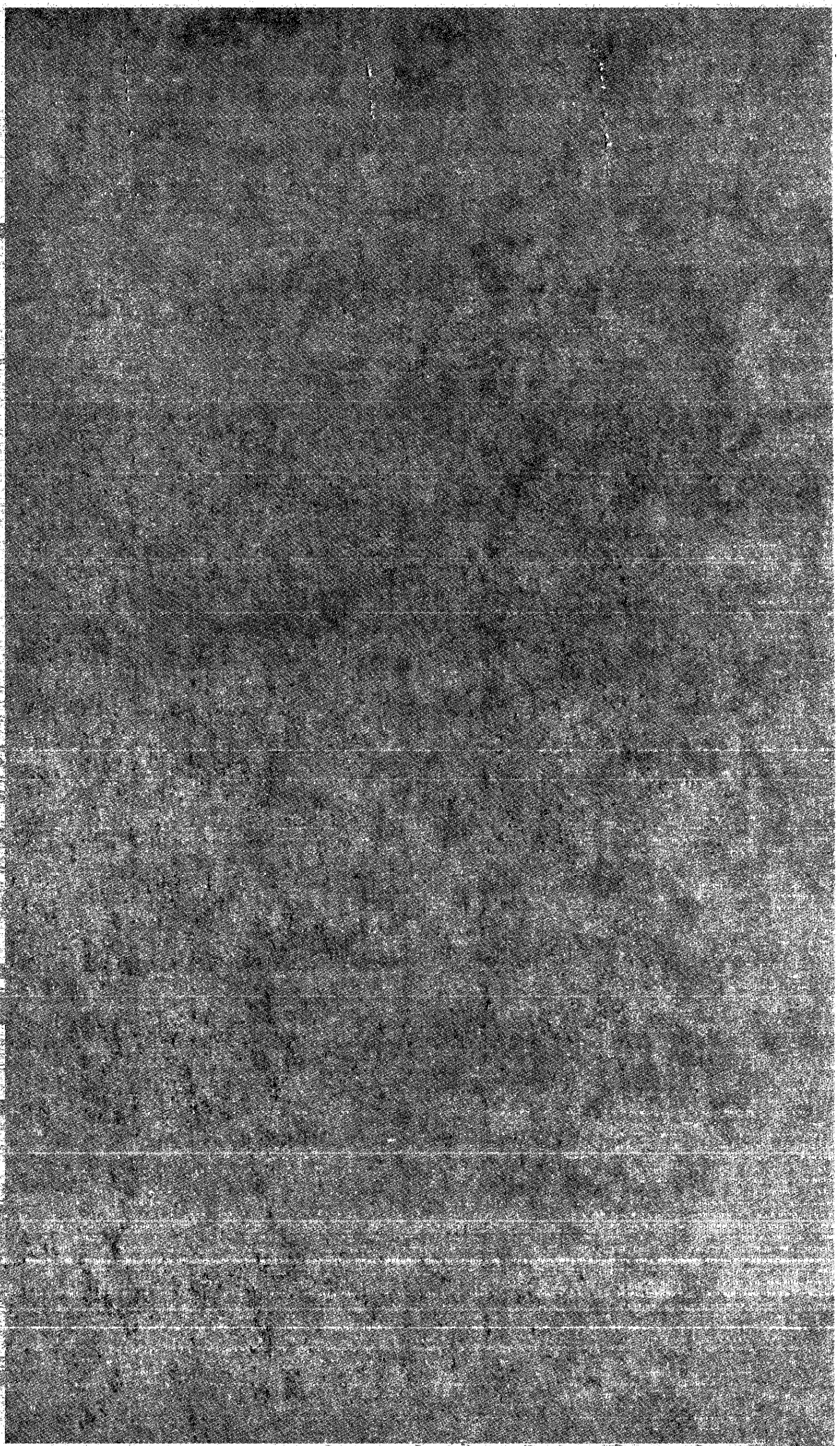

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