
Contributed Papers

MINIMIZING THE SOURCES OF ERROR IN THE ANALYSIS OF GEOLOGICAL SAMPLES BY X-RAY FLUORESCENCE

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Introduction

X-ray fluorescence spectrometry (XRF) has generally been the method of choice for the last few decades for the analysis of geologic samples, particularly for major element analyses of silicate rocks. It offers high precision (typically less than 1 % relative standard deviation (RSD) for the major elements) with minimal sample preparation and analysis times. A given rock can be crushed, fused or pressed, and analyzed on an "as received basis" within two hours if need be. The same sample preparation can also provide information on some ten to twenty trace elements with detection limits normally well below 100 ppm if the XRF analysis time is increased from the 15 minutes it takes for major elements to one to two hours per sample. An introduction with the basic steps involved in setting up the Rigaku model 3070 for a silicate rock analysis has already been published in this journal [1].

However, the high precision in a very reasonable analysis time does not translate into an equivalent degree of accuracy, a fact which is difficult to transmit to the customer who always sees analyses totaling to $100.00 \pm 0.10\%$ in the literature. Although it is possible to obtain accuracies in the tenths of a percent, a much more time consuming process is required than was usually employed, and currently no "miracle cures" exist. Even if only basaltic rocks are to be analyzed, geological analysis labs, the samples are rarely routine because standards that have essentially equivalent compositions even to the trace components do not exist. Even if only basaltic rocks are to be analyzed, the variability between samples is too great to expect the major components to al-

ways be within a few tenths of the true or even the accepted values.

Just how bad is the accuracy for routine analyses? How much precision and accuracy should be expected for how much effort? What can be done to obtain the best answers, if those are really needed for the problem at hand? These are important questions which must be addressed when protocols are being written or when consumers of the information being generated aren't thinking in terms of cost/benefit curves. These are also the questions we would like to address here, using geological analyses as our primary focus, although the answers are also important to other sample types such as powdered biological materials (which we also do in our laboratory).

Instrumental Errors

The total error of an analysis can be calculated by a simple summation of the contributing errors (as variances) if they are known and if they are independent of each other. If they are not independent, the covariance terms should also be included. Fortunately, the sampling, instrumental, and calibration errors are generally independent of each other, though an experimental design which tests for this may be employed if there is any doubt [2]. The contributing sources of instrumental error are also usually independent of each other, and these have been taken up in detail elsewhere [3]. For our purposes here we need only note that there are always fundamental noises (shot or counting statistic noises, equal to the square root of each signal N), nonfundamental noises (usually a drift or flicker symbolized here by ξ), and various kinds of reset and positioning errors (symbolized here by ϵ). The precision

(RSD) of the sample analysis can then be calculated from Eq. (1)

$$RSD_{sample}^2 = N_{pk}^{-1} + N_{bkd}^{-1} + \mathbf{x}_{drift}^2 + \mathbf{e}_{reset}^2 + \mathbf{e}_{position}^2 + \mathbf{e}_{sampling}^2 \quad (1)$$

The individual symbols are defined in Table 1. For the purposes of this work,

$$\mathbf{e}_{sampling}^2 = \mathbf{e}_{preparation}^2 + \mathbf{e}_{subsampl}^2 + \mathbf{e}_{fieldsampl}^2 + \mathbf{e}_{calibr}^2 \quad (2)$$

The sampling error is not an instrumental error, and it will be taken up in more detail below. Combining Eqs. (2) and (3) and substituting the symbols defined in Table 1 gives us

$$RSD = \left\{ \frac{(r_p t_p + r_b t_b)}{(r_p t_p - r_b t_b)^2} + \frac{(r'_p t'_p + r'_b t'_b)}{(r'_p t'_p - r'_b t'_b)^2} + (\mathbf{x}_1 n t)^2 + (3n \mathbf{x}_2)^2 + 2(\mathbf{e}_3)^2 + (\mathbf{e}_4)^2 + (\mathbf{e}_5)^2 + (\mathbf{e}'_5)^2 + (\mathbf{e}_6)^2 + (\mathbf{e}'_6)^2 + (\mathbf{e}_7)^2 \right\} \quad (3)$$

For instruments that have a computer-controlled tube voltage and current, we would also have a term $n\epsilon_1$ that would be the reset error if the voltage or current is changed and then reset between, the sample and standard. This would not generally be done, as it would increase the instrumental error unnecessarily. Usually the background signals are counted for the same length of time as the peak signals for the sample and reference standard, so $t_p=t_b=t'_p=t'_b=t/2$. For the Rigaku sample changer in our instruments, $n=6$. If we also let ϵ_T be the sum of the individual ϵ 's, we can simplify Eq. (3) to give Eq. (4):

$$RSD = \left\{ \frac{1}{t} \left(\frac{r_p + r_b}{(r_p - r_b)^2} + \frac{r'_p + r'_b}{(r'_p - r'_b)^2} \right) + 36t^2 \mathbf{x}_1^2 + \mathbf{e}_T^2 \right\}^{1/4} \quad (4)$$

Note that there are three major terms in the expression: a first one, which is inversely proportional to the square root of the time spent on the analysis; a second one, which is directly proportional to the time spent on the analysis and which corresponds to an instrument drift; and a final term, which is independent of the time spent on

Table 2 Experimentally determined values for the factors in Eq. (5).

Factors	Buchanan and Tsai (1974)	Pupp (1977)	This work
ξ_1	1.3×10^{-7}	1.8×10^{-7}	1.4×10^{-7}
ϵ_1	4.3×10^{-3}	2.9×10^{-3}	1.1×10^{-3}
ϵ_2	1×10^{-7}	8.2×10^{-3}	$< 10^{-8}$
ϵ_3	2×10^{-3}	3×10^{-3}	1×10^{-3}
ϵ_4^a	6.8×10^{-3}	...	10^{-3}
ϵ_4^b	10^{-2}
ϵ_5	5×10^{-3}
ϵ_6	5×10^{-3}
ϵ_6^c	10^{-3}
ϵ_6^d	10^{-1}
ϵ_7^c	10^{-3}
ϵ_7^d	10^{-1}

a Single operator; standards and unknowns prepared on same day.

b Multiple operators; standards prepared on different days.

c Major oxides.

d Trace elements.

the analysis. Typical values for the parameters in the equations are presented in Table 2. Usually the first term is limiting at low concentrations. Therefore the detection limit is equal to two times the square root of the background count rate divided by the responsivity and the square root of the count time. This is the same as the equation derived elsewhere [4], but unfortunately it is often used as the limiting error even for intermediate concentrations so that users equate improved precision with improved accuracy. Longer counting times will not produce better results when the second and third terms are limiting.

A more conservative estimate of the detection limit makes use of the Student's statistic,

$$C_1 = (t_{\alpha/m})(2r_b/t n_m)^{1/2} \quad (5)$$

where t_{α} is the one-sided t statistic with $(\alpha = 0.05)$ and with degrees of freedom = $n - 2$: n is the number of standards used to get the calibration curve, n_m is the number of times the entire calibration curve process is repeated, usually once, and the other terms are defined in Table 1. If spectral overlaps exist, a more involved expression results, which has been presented elsewhere [3].

The second term in Eq. (4) is also generally not a source of significant error if care is taken. Rarely will a given sample be counted so long that the instrument's source or detector will drift enough to be a limiting source of error. More commonly, this term is limiting when calibrations

from one day are used days or weeks later. This problem is minimized by using an intensity reference and updating each tray load of samples. For fundamental parameter methods this is usually all that is required. However, for calibration curve methods it is wise to also periodically rerun the calibration with all of the different standards. Though it would not seem at first as if this should be necessary, apparently the source intensity and detector response do not change equally for all energies over time. If the matrix corrections have been obtained empirically, they may change slightly over time, making recalibration useful for the most accurate work.

The last term is the one usually limiting for major component analyses. However, the instrumental contribution to ϵ_T , such as reset errors for the goniometer and disk placement are not usually limiting unless the instrument is badly worn or needs oiling or unless the disk is not homogeneous, and these problems are usually very apparent. On the other hand, the sample preparation, sampling, and calibration error contributions to ϵ_T are very important, and it will be useful to look at these in more detail.

Sample Preparation Errors

Errors in obtaining a representative sample in the field or even from a subsample in the laboratory are particularly difficult to eliminate. A variety of approaches for minimizing these errors exist, and if they are a problem it is worthwhile referring to a treatise devoted to the topic [5]. Caution must also be exercised in preparing and pulverizing the sample to avoid contaminations [6,7]. Tungsten carbide mills, for example, introduce enough cobalt from the binder to be detected by XRF. It is a good practice to grind some of the sample and discard it in order to clean the apparatus before grinding the aliquot that is to be analyzed.

Once a representative, uncontaminated powder has been obtained, a number of options are available for preparing the sample for placement in the X-ray beam, each with its own advantages and disadvantages. The three most common methods have been pressed powders, glass disks made by fusing with a borate, and glass disks made by fusing with a borate doped with a heavy element compound such as lanthanum oxide. The heavy element serves to equalize the mass absorp-

tion coefficients between samples and standards, making calibrations more linear.

Pressed powders were popular in the early days of XRF analysis of geological samples, but the bad matrix and particle size effects lead to the ascendancy of the borate fusion methods. The matrix effects may now be correctable with appropriate computer programs, but the particle size effect can still affect the accuracy and precision of the analysis. Pressed powders may still be preferable for trace element analyses because the more concentrated samples give about a factor of two or three lower detection limits for equivalent counting times. In Table 3 data from an earlier paper is presented for detection limits obtained using different dilution methods [8]. Note that for a 10:1 dilution without heavy element doping counting ten times as long duplicates the detection limits obtained with the pressed powder and binder. As the diluted samples have lower matrix interactions, the accuracy of the fluxed samples is expected to be better than the pressed powders unless matrix corrections are employed. Matrix corrections are generally limited to the effect of the major components, although overlap corrections are often necessary for trace elements.

Pressed powders are also preferable if the fluxing method introduces an error, such as in the analysis of volatile elements or compounds. Because of the volatility of the compounds present, biological samples are usually analyzed as powders after packing them into sample cups [9, 10]. Binders may be avoided by using mylar films over the cups. A second problem can be the solubility of a component in the flux. For example, lithium

Table 3 Detection limits (ppm) for the various sample preparations.

Element	Glass disk			Pressed powder
	50:1 dilution	10:1 dilution	3.5:1 dilution	7:5 dilution
Ba	200	100	22	36
La	100	48	16	17
V	50	12	5	8
Ce	135	63	22	28
Cr	42	14	3	4
Co	47	13	5	6
Ni	78	25	6	4
Zn	34	14	5	6
Rb	55	13	4	6
Sr	50	12	4	3
Y	61	14	5	3
Zr	45	11	4	5
Median	53	14	5	6

tetraborate is not basic enough to readily dissolve Fe_2O_3 , so that iron analyses with glass disks made from it sometimes have less precision than would be expected. The iron is expected to be more soluble in the +2 state than in the +3 state, so it is tempting to add a volatile reducing agent to the flux to increase the dissolution of the iron compounds. However, many elements can react with the platinum crucible usually employed, so that it is normal to add an oxidizing agent, such as NH_4NO_3 instead.

Other problems for the fluxing methods include the hygroscopic nature of the borate powders. This is not much of a problem for the pre-fused, ground, and sieved powders of lithium tetraborate sold by companies such as Spectromelt. The sieving removes the very fine particles that tend to form an irritating dust and decreases the surface area available for water adsorption during weighing. The heavy element doping may also present problems, as La_2O_3 is even more hygroscopic than the flux. Also, although lanthanum is not generally thought to be particularly toxic, it is a known calcium antagonist, and when lanthanum compounds are injected into rats, the lethal dose is essentially the same as for comparable lead compounds.

Like pressed powders, the use of a heavy element doping agent has also been somewhat supplanted as more complex matrix correction programs have been developed with faster computers, making the use of a heavy element absorber unnecessary. In fact, Table 4 illustrates that there seems to be little or no advantage to the use of heavy element doping, as dilution with nine parts lithium tetra borate to one part rock powder gives equivalent or better precisions and accuracies for the elements studied. The data in this table was obtained using a fundamental parameters program (J. Criss Software, Inc., 1979) for the undoped samples, and the method of Norrish and Hutton [11] for the lanthanum-doped samples using a Rigaku model 3064 XRF. Details of the parameters used in the study are given elsewhere [8], but they are essentially those given in the experimental portion of this paper.

There is reason to believe that regression methods without matrix corrections would be improved by the use of a heavy element absorber, as it should make the mass absorptions of different samples more equivalent. However, more sample

Table 4 Major oxide and trace element average relative standard deviations (%) for different sample preparations.

Oxide element	Glass disk			La doped 6.4:1 dil.
	50:1 dil.	10:1 dil.	3.5:1 dil.	
Na_2O	3.4	2.5	2.4	2.1
MgO	2.6	2.1	2.3	3.4
Al_2O_3	1.6	1.2	2.9	1.1
SiO_2	1.4	0.7	2.5	0.4
P_2O_5	0.5	2.3	3.4	2.0
K_2O	2.8	2.3	0.8	2.0
CaO	2.5	1.0	3.0	2.0
TiO_2	4.3	4.4	6.1	2.5
MnO	2.9	4.0	3.3	5.0
Fe_2O_3	2.0	1.7	2.9	3.4
Average	2.40	2.22	2.96	2.57
Expected error in the total	0.93	0.51	1.74	0.46
Element				Pressed powder, 7:6 dil.
Ba	7	10	10	12
La	10	10	10	15
V	5	13	15	14
Ce	22	13	10	13
Cr	7	4	5	9
Co	12	6	6	6
Ni	6	5	4	6
Zn	8	6	6	3
Rb	7	3	6	4
Sr	6	5	5	5
Y	6	6	6	7
Zr	10	7	6	7
Average	8.8	7.3	7.4	8.4

is also used in order to get count rates back up, which in turn makes the matrix effects worse again, canceling some of the gains made. Dilution also tends to equalize the mass absorption coefficients, and, at least in theory, allows less sample to be used. In practice, both dilution and doping methods usually use about a gram of rock powder in the analysis and a combination of dilution and doping together with longer count times is probably best employed to give the most linear calibrations in the absence of adequate matrix corrections. The one-gram sample size is convenient for handling, and the relative error due to moisture adhering to the flux and sample during weighing goes up as less sample is used. For one gram samples, % RSDs of less than 1 % are typically obtainable.

Calibration Method Errors

The number of different methods for calibrating the relationship between the intensity and the concentration of an analyte in the sample is at least as great as the number of different sample preparation methods. However, for simplicity we

can lump these into the empirical methods and the fundamental parameters methods. Although there is a fair amount of overlap in how the two methods are calculated and employed, generally the empirical methods require a series of standards which are similar in the bulk matrix to the unknown sample(s). The fundamental parameters methods, on the other hand, usually make use of a single standard to calibrate the X-ray beam intensity. Fundamental information about the spectrometer geometry and the absorption and fluorescence enhancements expected for the elements being analyzed is then used in an iterative calculation that closes in on the true composition. Both methods are more accurate the closer the standard(s) are to the sample in composition, and the greatest accuracy would be obtained in a "null" method in which the analyst prepared standards that duplicated the samples' composition and then reanalyzed them all, provided no additional errors were introduced in the preparation of the new standards. As trace element contaminations are often present in even reagent grade standards, this is a greater concern than might at first appear to be true [6].

Some good studies have been done comparing the various fundamental parameter and empirical methods [12-16], usually based on the theoretical work of Sherman [17,18]. However, none of these specifically addressed the range of concentrations and the set of elements we have been encountering in our geological analysis laboratories. Users are interested in not only silicate rocks, but also sedimentary (which sometimes contain fossil bones to be analyzed), mineral ores (where care with the platinum must be taken), and metamorphic rocks. These are all routinely prepared using a 9 or 10:1 dilution, undoped, fused borate glass disk. Consequently, we selected a wide range of sample types from the NIST (the new name for the NBS) covering cements, bauxites, and phosphate, silicate, and carbonate rocks. We wished to compare the simplest of regression procedures without matrix corrections with a complete fundamental parameters method to see how much of an error the calibration method introduces, and how much can be readily corrected in a routine analysis.

Experimental

Duplicate disks of each rock standard were

prepared using 1.000 g samples of the NIST standards fused with 9.000 g of prefused, ground, and meshed lithium tetra borate available commercially (Spectromelt) in 95% Pt/5% Au crucibles (Englehard) at 1150°C with a Meeker burner using propylene and air for 15 minutes with shaking on a Junior Orbit Shaker (Lab-line Instruments) set to 200 rpm. The melt was checked for completeness of the dissolution and returned for an additional 10 minutes if residual particulates were present. The melt was then poured into 3.5 cm diameter Pt/Au molds which were heated to 800°C over a bunsen burner to remove the need for a wetting agent. The molds were promptly removed from the burner and placed on an aluminum block to cool the melt rapidly, ensuring the formation of a glass. After the glass pulled away from the mold, the disks were inverted on a 100°C hot plate to slowly cool, reducing the incidence of cracking of the disk. (Using this procedure, only about one in fifty disks will crack, usually due to a very small, undissolved particle.)

Duplicate analyses of each disk on each instrument were then conducted using a Rigaku model 3070 for the simple regression based analyses, and a Rigaku model 3064 for the fundamental parameters based analyses. The fundamental parameters package used was that available from J. Criss Software, Inc. (1986), which was run on a DEC micro-VAX III computer connected directly to the 3064. The instrumental conditions summa-

Table 5 Parameters used in the analysis of major and trace elements in undoped, fused-glass disks of silicate rocks and minerals.

Oxide	Analysis crystal ^a	Peak time ^b	Peak 2θ	Background 2θ's	
Na ₂ O	TAP	40	55.14	53.00	56.30
MgO	TAP	20	45.19	43.00	48.00
Al ₂ O ₃	TAP	20	37.81	34.30	40.35
SiO ₂	PET	20	109.04	105.00	112.00
P ₂ O ₅	PET	20	89.47	87.00	91.00
K ₂ O	LiF	20	118.13	117.00	120.13
CaO	LiF	20	113.09	111.30	115.30
TiO ₂	LiF	40	86.17	84.50	88.00
MnO	LiF	20	62.96	62.00	64.70
Fe ₂ O ₃	LiF	20	57.50	59.00	56.00

a Elements lighter than Ca were analyzed using the FPC

b Count times used for each of the backgrounds were half those used for the peak. Total analysis time is 8 minutes, not counting the time for goniometer movement, etc. Users often select a repeat count to be assured they are not limited by counting statistics, especially for lower concentration samples.

Table 6 Comparison of weight percents of oxides in NIST standards using linear regressions and fundamental parameters versus literature values [19].

Oxide	1c	98A	99A	278	634	688	694	698	1646	1883	2691	4355
Regressions:												
Na ₂ O	0.01	0.08	6.08	4.85	0.14	2.10	0.54	0.09	2.52	0.32	1.40	2.73
MgO	0.53	0.47	0.01	0.27	3.14	8.86	0.44	0.09	1.75	0.38	5.04	1.88
Al ₂ O ₃	1.30	33.17	19.91	13.96	4.91	17.95	1.81	48.58	11.51	70.53	17.65	15.29
SiO ₂	7.08	48.19	64.92	73.62	20.49	50.15	11.06	0.70	67.16	0.34	35.63	62.72
P ₂ O ₅	0.05	0.12	0.01	0.02	0.12	0.12	30.17	0.35	0.08	0.011	0.99	0.20
K ₂ O	0.27	1.09	5.09	3.99	0.42	0.23	0.55	0.03	2.33	0.004	0.43	2.30
CaO	55.06	0.32	2.00	0.94	60.62	12.53	41.54	0.66	1.16	26.93	25.16	3.31
TiO ₂	0.50	1.55	0.01	0.20	0.18	1.07	0.08	2.47	0.69	0.01	1.19	0.70
MnO	0.025	0.007	0.002	0.06	0.17	0.16	0.014	0.41	0.055	0.001	0.024	0.11
Fe ₂ O ₃	0.42	1.54	0.07	2.04	2.09	9.60	0.37	20.00	5.27	0.33	5.78	5.44
Fundamental Parameters using JB-1												
Na ₂ O	0.00	0.05	4.92	4.42	0.11	1.89	0.91	0.04	2.08	0.025	1.30	2.22
MgO	0.34	0.19	0.00	0.08	3.29	9.27	0.28	0.00	1.70	0.00	5.22	1.81
Al ₂ O ₃	1.33	33.63	20.46	14.19	5.05	18.13	1.90	51.26	11.78	70.75	17.52	15.68
SiO ₂	7.37	49.62	63.89	73.65	20.73	49.97	11.31	0.79	65.83	0.45	34.89	62.06
P ₂ O ₅	0.10	0.11	0.01	0.03	0.17	0.14	30.30	0.38	0.12	0.04	1.15	0.23
K ₂ O	0.29	1.11	5.17	4.20	0.44	0.23	0.55	0.03	2.28	0.05	0.42	2.31
CaO	54.66	0.35	2.11	1.07	61.77	12.99	43.09	0.66	1.25	26.53	76.99	3.41
TiO ₂	0.09	1.75	0.01	0.25	0.30	1.23	0.13	2.60	0.87	0.01	1.54	0.81
MnO	0.03	0.00	0.00	0.05	0.25	0.17	0.01	0.42	0.05	0.00	0.02	0.10
Fe ₂ O ₃	0.97	1.47	0.12	1.84	2.72	10.23	0.94	21.32	5.53	0.40	6.86	6.00
Fundamental Parameters using NIST 639												
Na ₂ O	0.01	0.07	6.58	6.15	0.15	2.62	1.22	0.06	2.78	0.34	1.80	2.98
MgO	0.34	0.19	0.00	0.074	3.30	8.68	0.28	0.00	1.70	0.00	4.89	1.82
Al ₂ O ₃	1.37	34.71	21.16	14.16	5.22	18.04	1.97	52.95	12.17	73.01	17.44	16.20
SiO ₂	7.54	50.82	65.62	74.81	20.77	50.66	11.62	0.80	67.46	0.46	35.39	63.60
P ₂ O ₅	0.06	0.06	0.01	0.021	0.10	0.10	29.82	0.23	0.07	0.32	0.81	0.14
K ₂ O	0.28	1.06	4.95	3.93	0.42	0.22	0.51	0.02	2.18	0.05	0.40	2.21
CaO	55.75	0.36	2.14	1.06	63.01	12.87	43.59	0.67	1.27	27.07	26.72	3.47
TiO ₂	0.09	1.72	0.01	0.257	0.29	1.25	0.13	2.56	0.86	0.01	1.56	0.80
MnO	0.03	0.00	0.00	0.064	0.28	0.20	0.02	0.47	0.05	0.00	0.024	0.12
Fe ₂ O ₃	1.03	1.57	0.13	1.65	2.90	9.23	1.04	22.74	5.89	0.43	6.19	6.39
Consensus values												
Na ₂ O	0.01	0.082	6.14	4.72	0.15	2.09	0.86	0.015	2.75	0.32	1.47	2.59
MgO	0.42	0.42	0.02	0.25	3.30	8.72	0.33	0.055	1.61	0.29	5.17	2.49
Al ₂ O ₃	1.3	32.92	20.41	14.38	5.10	17.33	1.80	47.44	10.47	71.2	18.54	15.48
SiO ₂	6.84	47.51	65.1	71.44	20.48	48.17	11.19	0.68	64.20	0.35	36.00	70.6
P ₂ O ₅	0.038	0.11	0.013	0.032	0.10	0.16	30.16	0.36	0.11	---	1.17	0.25
K ₂ O	0.28	1.04	5.12	4.07	0.42	0.19	0.51	0.010	2.20	(0.01)	0.40	2.24
CaO	50.3	0.31	2.11	1.00	63.0	11.85	43.68	0.62	1.18	27.8	25.81	3.08
TiO ₂	0.07	1.61	0.007	0.24	0.29	1.18	0.11	2.34	0.70	(0.01)	1.50	0.78
MnO	0.025	0.005	---	0.050	0.28	0.156	0.012	0.37	0.043	---	0.026	0.11
Fe ₂ O ₃	0.56	1.26	0.068	2.09	2.84	10.25	0.79	19.45	4.60	0.08	6.32	6.36

alized in Table 5 were selected using Eq. (I) to obtain the optimum analysis times for each element. Absorbers were used to keep some elements in the linear region of the detector for the 3064, but they were not used for the 3070. (Conditions used for the 3064 have been presented before [3].)

For both the linear regression and the fundamental parameters methods, two approaches were taken. The 3070 regressions were first run simply using the standards presented in Table 6 using background subtracted intensities versus the consensus concentrations [19]. Standards were also

prepared using analytical reagent grade chemicals as a check of the accuracy of the curves prepared from the rock standards. Ideally, the rock standards would be the unknowns, but as they are more readily available to the general public and the trace element composition is better known, the convention seems to be to create calibration curves from the rock standards rather than from the chemical reagents themselves. This makes the data appear somewhat better than it really would if the rock standards were a complete unknown, though the difference in the RSD's should not be

significant.

The rock standards were also regressed using the logs of the intensities versus the logs of the concentrations. This served to weight the various concentrations equally, extending the dynamic range more accurately to the low concentrations. These results were then combined. The final concentrations reported here are those calculated from the un-transformed linear regression for those concentrations greater than the mean concentration of each element, and from the log transformed linear regression for those concentrations less than the mean concentration for each element. Again, no matrix corrections were calculated for these regression calibrations, though some improvements could be obtained in at least Ca and Fe by using matrix correction models.

For the 3064, two different standards were used as the starting point for the fundamental parameters program. In the first case, a basalt (JB-1) was used to calibrate the method, and in the second a cement (clear, or NIST-639) was used. The two are widely disparate in composition so that closure on the actual concentrations for the unknowns will be achieved following different paths. This should serve as a check on the accuracy of the fundamental parameters method.

Results

In Table 6 the results of the analyses are presented. The first analysis presented is that for the combined regression method; the second is for the fundamental parameters method using JB-1 (a basalt) as the starting model for the program; the third is for fundamental parameters using NIST-639 (a cement) as the starting point; and the last are the consensus values reported in 1987 by Gladney et al. [19]. These values are generally the

same as the NIST certificates of analysis, but when sufficient data has appeared in the literature, these values may be considered to be superior.

In Table 7, the average deviations and average relative deviations (as a percent) for each of the methods are presented. The calibration curve method is not as good as the fundamental parameters method for Ca and Ti, as was expected due to the increased interaction and matrix effects for these elements. However, the difference is not very large, and for the lighter elements the calibration method pulls ahead, especially for sodium. For these elements, matrix effects are less pronounced and the two methods should be equivalent (and probably would be if the calibration method were done on standards external to the rock standards).

It is worth noting in Table 6 that the fundamental parameters method does very well on those samples closest to the initial starting point. For example, gold cement (NIST -634) has a very similar composition to clear cement (NIST -639), and the agreement between the consensus values and those obtained by the fundamental parameters program starting with clear cement are excellent, as would be expected. This is very nearly the "null" method mentioned earlier for obtaining the best accuracy in any analysis. For the basalt 688, the agreement is not nearly as good, partially because the starting point (JB-1) is not as close in composition to 688 as the clear cement is to the gold cement, and partially because the 688 disk appears to have a slightly higher ratio of rock powder to flux than is expected. As 688 and 278 were prepared at a different time with a different batch of flux by a different operator than the rest of the data, it is instructive to leave them into

Table 7 Average deviations and relative average deviations for various calibration methods

Oxide	Regression method		Fund. Param. (Basalt)		Fund. Param. (Cement)	
	Ave. Dev.	Rel. Dev.	Ave. Dev.	Rel. Dev.	Ave. Dev.	Rel. Dev.
Na ₂ O	0.09	39	0.27	32	0.30	34
MgO	0.13	21	0.19	42	0.19	48
Al ₂ O ₃	0.49	2.8	0.73	3.8	1.22	6.1
SiO ₂	1.39	3.0	1.65	7.1	1.84	8.2
P ₂ O ₅	0.03	101	0.03	350	0.03	360
K ₂ O	0.04	26	0.05	55	0.04	44
CaO	1.00	5.0	0.86	6.2	0.74	6.5
TiO ₂	0.11	62	0.06	9.1	0.06	8.9
MnO	0.016	23	0.011	36	0.017	43
Fe ₂ O ₃	0.44	41	0.44	54	0.64	62

show the variability possible even when the same protocol is being used. The variability in preparation, although less than the variability between calibration methods, is still significant. As was noted in Table 2, it appears to be about 1%.

In Table 7 the relative average deviations are a little less than 5% for the major components, but are as great as 20 to 40% for the minor components. These rather grotesque errors are due to a variety of correctable problems. These include: 1) the concentrations of these minor components are rarely reported in the literature to as many significant figures as the major components (or even the trace elements!); 2) counting times used are often inadequate for determining the minor components accurately; 3) the calibration methods, especially regression methods, do not weight these points as heavily as the larger concentrations. They also may be farther from the starting points for the fundamental parameters methods, leading to greater errors. The log transformations used in the regression based calibrations presented in the first part of Table 6 are clearly superior for determining the lower concentrations, as was expected. Hence, the combined regression method produces lower overall relative errors than even the fundamental parameters method. Intermediate matrix corrected methods, such as the Rasberry-Heinrich [12], would be expected to perform similarly to a complete fundamental parameters method for the major elements, though possibly not quite as well. Such hybrid methods might be expected to be better than the fundamental parameters but worse than a log transformed regression for the low concentration elements, depending on how the weighting is done. Thus, most of the algorithms will probably produce similar results, and the best approach would be to run a variety of algorithms that start with different assumptions and examine the assumptions to see if they hold in the region of interest. For those that do, a median of the results should give a fairly accurate value.

The convention of using regression methods on rock standards is also subject to some question statistically as the rock standards should be independent of each other in order to really qualify as separate standards. However, because they are composed of a limited number of minerals that tend to correlate the elements together, even the disparate NIST standards presented in Table 6 represent only four different compositions in a

statistical sense. (This can be verified readily with a cluster analysis of the standards.) This presents a problem when using such standards to calculate influence coefficients. It is very easy to be fooled as regression programs assume the standards are independent of each other and they will give coefficients that allow the data to be matched very nicely. For example, using the Rasberry-Heinrich model [12], which has been shown to be questionable on a theoretical basis [14], it is possible to get a correlation coefficient (r^2) of 100% for Ca with absorption corrections for Al, Si, and P, and enhancement corrections for Ti, Mn, and Fe using the data in Table 6. Because there is not enough independent information in the data table, the coefficients obtained are not really to be trusted despite how well things seem to be working.

To completely calculate linear corrections for all possible interactions for ten elements in a full factorial design would take 210 or 1024 different disks! Fortunately, many of the interactions are known to be zero, and it is possible to use fractional factorial experiments that will produce the needed coefficients in about twenty-four experiments, if the element combinations are designed properly. That means that only about twenty-four disks need to be prepared to determine accurate calibration curves with matrix corrections, but the concentrations of the elements in the disks cannot be randomly selected. Nor should they be just whatever is available in rock standards. It is quite possible that some of the instability found in the empirical models or calibrations when they are applied to new samples outside of the range of the initial calibration is due to inadequate selection of standards. By carefully selecting rock standards and mixing them together in various proportions in a generalized standard addition approach, it should be possible to construct a set of well-characterized hybrid standards that correctly adjust for matrix effects over a wide range of concentrations.

Conclusions

Before closing, it is worth noting that the 2-5% relative deviations (for the major components) are essentially equivalent to those reported in the literature for every approach except the "null" method. Even the standardless, semi-quantitative analysis, fundamental parameter method based on a sensitivity library now available on the Rigaku

3270/3271 and 3370/3371 sequential spectrometers [20] does this well! In order to get better than these relative deviations, some version of the null method must be employed, either through matching of the sample to a similar known using a priori knowledge about the sample, or by re-running the sample with a standard made up to have an equivalent concentration after determining its initial concentration using a fundamental parameters program or a combined regression analysis on a diluted sample as was conducted here. By using the instrument parameter optimization represented by Eq. (6), and by using an iterative approach to the preparation as well as calibration step, errors may be reduced to the few tenths of a percent the technique promises, and the public expects!

Acknowledgements The authors would like to thank E. S. Gladney for providing many of the NIST standards used in this study, and for generous grants from the Otis and Margaret Barnes Trust fund and the Keck Foundation which made this work possible.

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