

A simple method for quantitative analysis of elements by WD-XRF using variable dilution factors in fusion bead technique for geologic specimens

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A common approach in the quantitative analysis of geological samples by X-ray fluorescence is to establish calibration lines for elements of interest by using several reference materials (RMs) and/or the combination of RMs and pure chemicals. Herein, we introduce an alternative to use only two RMs, to establish a calibration application. Variation of the dilution factor is employed to generate a dynamic range of concentrations for each RM and to evenly furnish the calibration lines to analyze certain matrices. A wide range of dilution factors were employed from 2–54 times dilution (with respect to the flux to sample ratios). Calibration lines for the major elements including: Si, Al, Ca, Fe, Mg, Na, Mn, and Ti show an extremely high level of linearity with all elements. R^2 values greater than 0.9990 were obtained for each analyzed element. The calibration application was validated by checking against a variety of geological RMs including petroleum and carbonate rich shale (SGR-1), Muscovite rich marine shale (SBC-1), metamorphic rock (SDC-1), carbonatite (COQ-1), and types of igneous rocks (GSP-2, BCR-2, AGV-2, QLO-1, and W-2). Mixtures of Alumina and Silica (ARG-1 and ARG-2) and pure SiO_2 beads were also analyzed to further check the application. Rigorous statistical analysis on the RMs confirms the reliability of the calibration application for the employed matrices. Copyright © 2016 John Wiley & Sons, Ltd.

Introduction

X-ray fluorescence (XRF) spectroscopy is a mature technique in the quantitative elemental analysis of conventional matrices such as: geological,^[1] cements,^[2] and mining^[3,4] specimens. In addition, the ease, speed, precision, and reproducibility of XRF have extended its applications to a wide range of other samples such as water and wastewater,^[5] catalysts,^[6] thin layers and semiconductors,^[7,8] and lubricants.^[9]

Although the instrumentation is precise and accurate, sample preparation can be a major source of error because of the complexity and heterogeneity of naturally occurring geologic specimens.^[10] The two main methods of sample preparation are pressed pellet and fusion bead. Each of these has its inherent advantages and constraints in terms of accuracy, sensitivity, etc. The fusion bead approach provides the best homogeneity and resolves the mineralogical (matrix) effects, and thus, analysis is more reliable. However, the dilution of constituents lowers the sensitivity, which could be problematic for trace element detection. Generally, employing a low dilution factor has been a reasonable response to such concerns in the past.^[11–15]

Specimen preparation methods have been described in detail, in a review paper, by Blank and Eksperiandova (1998).^[10] Regardless of the method, to analyze a sample of interest, a calibration is required for quantitative analysis of the elements. When RMs or certified reference materials (CRMs) are unavailable, most XRF instruments are equipped with standardless analysis tools using the Fundamental Parameter (FP) method and a sensitivity library. However, results are rather semi-quantitative and need to be

re-ensured through a quality control process.^[16] When a more accurate elemental analysis is required the establishment of a calibration methodology is crucial. In most cases, scientists and spectroscopists employ a wide range of RMs from different sources; such as, the US Geological Survey (USGS) and the Geological Survey of Japan. The constituents of geological specimens cover a wide range of concentrations from a few $\mu\text{g/g}$ to 100%. Technically, in the establishment of a calibration method, the upper and lower limits of concentration are defined based upon the maximum and minimum available concentrations of an element in the reference material sample. Extrapolation beyond the range of concentrations of an element in a standard sample for an unknown sample is generally avoided as uncertainty likely increases beyond the limit range. Therefore, establishing many sufficient RMs (usually more than 10)^[17] to cover a wide range for each element is crucial. RMs are limited for such a purpose as they contain arbitrary composition, and they may result in a highly dispersed distribution of data points. To address this shortcoming, workers employ numerous RMs to cover a sufficiently wide range of concentrations. However, this approach can raise some concerns; such as the following: (1) fusion conditions, (2) diverse physical properties of the sample, and (3) X-ray spectra interferences.

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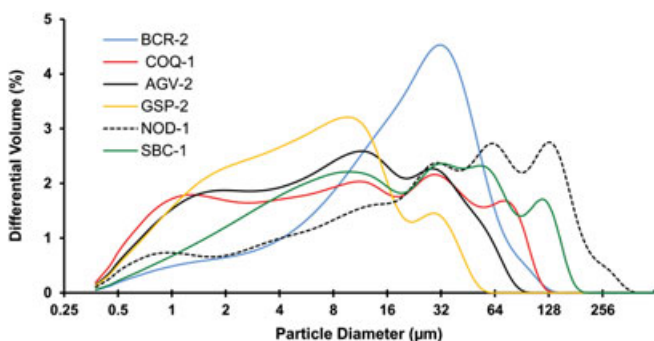


Figure 1. The particle size distribution curves of several US Geological Survey reference materials including SBC-1, NOD-1, GSP-2, AGV-2, BCR-2, and COQ-1. BCR-2 and COQ-1 were used to generate the calibration application. NOD-1 was shown for comparison only. Reference materials were analyzed by laser diffraction particle size distribution analyzer (Beckman-Coulter) at Argile Analytica Inc. facility.

Table 1. Statistical data of the particle size distribution of the four USGS RMs.

RM	BCR-2	COQ-1	AGV-2	SBC-1
Volume %	100	100	100	100
Mean P.S.* ^s	25.61	19.74	14.35	31.78
Median P.S.	21.11	8.41	7.78	14.94
Mode	34.58	31.50	12.39	34.58
% <	Size (µm)	Size (µm)	Size (µm)	Size (µm)
10	3.05	0.98	1.11	1.99
30	11.38	2.90	3.10	6.29
50	21.11	8.41	7.78	14.94
60	26.74	13.42	11.34	24.36
90	53.13	59.07	38.71	89.45

*P.S., particle size.
RSM, reference materials; USGS, US Geological Survey.

Usually, a single fusion condition (e.g. fusion temperature and time, type of flux, and melting point of minerals) for numerous RMs is likely unable to properly create a homogenous bead especially if the matrix varies widely. Using numerous fusion conditions will ultimately result in some inaccuracy.

Moreover, RMs are essentially different in their properties such as particle size distributions, hygroscopic nature, and variation of the standard deviation and uncertainties in reference values in the certificate of analysis. For instance, unlike most RMs, which only need to be dried at 110°C for 2h prior to use, NOD-1 needs to be dried for 24h at 110°C to ensure it is moisture free. NOD-1 can absorb up to 10% moisture due to the overnight exposure to the air (Fig. 1).

Table 3. Measuring conditions of the WD-XRF Supermini 200 for the selective elements of interest.

Element	Line	Crystal	Detector	Peak (2θ)	Bgd1 (2θ)	Bgd2 (2θ)	Corrected for
Na	Kα	RX25	PC	46.29	48.79	—	P
Mg	Kα	RX25	PC	38.06	40.8	—	Ca
Al	Kα	PET	PC	144.57	147.95	—	Ca
Si	Kα	PET	PC	108.92	—	—	Sr
P	Kα	PET	PC	89.34	91.7	—	—
K	Kα	PET	PC	50.61	49	—	—
Ca	Kα	PET	PC	45.15	47.9	—	—
Ti	Kα	LIF(200)	SC	86.12	84.94	—	—
Fe	Kα	LIF(200)	SC	57.48	55.58	—	Mn
Mn	Kα	LIF(200)	SC	62.94	64.16	—	—
Sr	Kα	LIF(200)	SC	25.12	25.82	24.28	—

WD-XRF, Wavelength-Dispersive X-ray Fluorescence.

When using numerous RMs in XRF, spectra overlap may also become a concern, as deconvolution or other overlapping corrections^[18] cannot be employed with reasonable confidence. One example is the spectral overlap between Mo Kα and Zr Kβ. When Molybdenum is the element of interest, substantial concentration of Zirconium makes it extremely difficult to measure Mo accurately.

Other methods to extend calibration lines include: using a mixture of pure chemicals,^[19,20] doping the (C)RM with a chemical containing the element of interest, blending two or more RMs, and using a secondary standard where the concentration of the elements are measured by different techniques such as Inductively Coupled Plasma, Atomic Absorption, or XRF. Nakayama and Nakamura^[17] have discussed the details of calibration standard fusion beads in geologic samples. These authors have explained that certified rock materials lose their reliabilities by blending with a chemical reagent as it cannot ensure analytical traceability. The rest of the aforementioned methods are common and practical in laboratory settings.^[17]

A common method in analytical chemistry, especially in elemental analysis by Inductively Coupled Plasma and Atomic Absorption, is to use a stable and concentrated standard with consecutive dilutions to obtain the desired range of concentrations. Normally, water or diluted acid are used as the solvent in such techniques. To the best of our knowledge, this approach has not been employed in XRF analysis, while geochemists and X-ray spectroscopists have shown great interest to use various types of RMs and secondary standards for quantitative analysis.

Herein, we examine the practicality of using the least number of RMs and varying the sample to flux ratio to obtain a controlled distribution of data points throughout the desired range of

Table 2. The dilution factors and actual masses used to prepare each glass bead.

RMs	BCR-2						COQ-1						
	a	b	c	d	e	f	g	h	i	j	k	l	m
Bead ID.													
RM mass (g)	0.200	0.500	0.846	1.000	1.570	2.200	2.750	3.666	0.500	1.000	1.570	3.000	2.750
Flux mass (g)	10.800	10.500	10.154	10.000	9.430	8.800	8.250	7.333	12.000	10.000	9.430	12.000	8.250
Dil. Factor	54	21	12	10	6	4	3	2	24	10	6	4	3

RM, reference material.

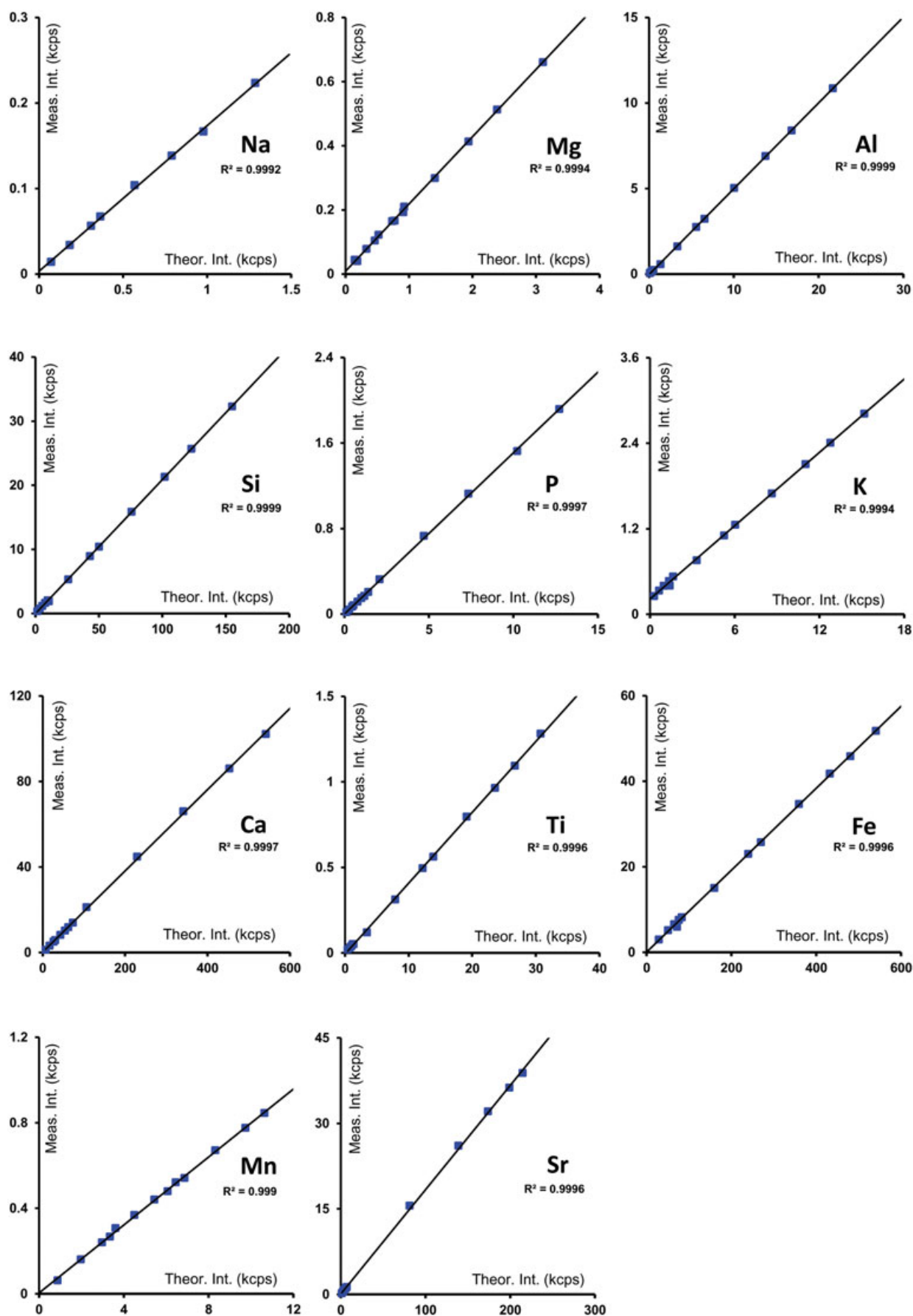


Figure 2. Calibration lines of 11 analyzed elements using the Fundamental Parameter method.

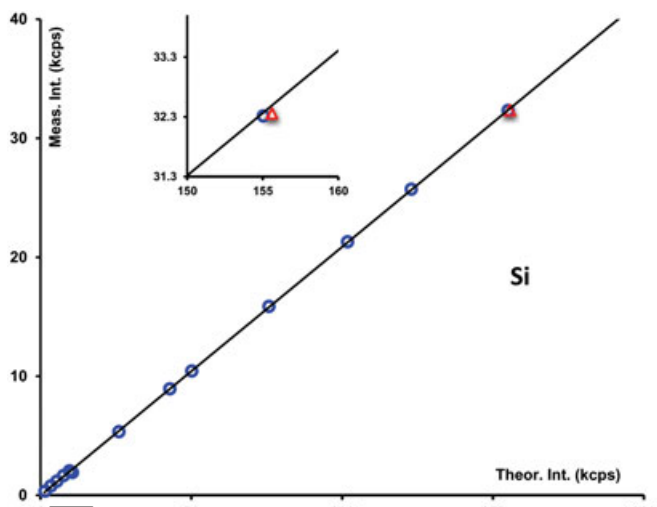


Figure 1. Calibration lines of 11 analyzed elements using the Fundamental Parameter method.

concentrations. The success of such an idea can introduce an alternative to the aforementioned techniques (various RMs, synthetic beads, etc.) to extend the calibration methodology. We emphasize that this method cannot succeed unless a proper specimen preparation been developed, being able to produce homogenous fusion beads over a wide range of dilutions especially at the low end, where the amount of flux is minimal with respect to the substrate powder. The major concern of this technique however is that any error from a poorly characterized RM may not be redressed since the number of RMs are limited, whereas in the case of using numerous RMs the bias in one RM can be canceled out by the values of remaining RMs. To minimize this effect, we recommend spectroscopists to use the most reliable RMs when the proper alternatives exist followed by a rigorous statistical analysis with sufficiently dynamic range of RMs to ensure the reliability of the calibration methodology. Further, variable dilution factors can be employed as one of the solutions in addition to the limited number of required RMs in order to retain the matrix similarity.

In sedimentary rocks, the concentration of SiO₂ can be as low as 5% in a carbonate rock and can be above 70% in clean sandstones. For example, the Montney formation in western Canada, from which specimens are routinely analyzed in our facility,

Table 4. The estimation of upper and lower limit ranges of concentration of each element in the calibration curves, assuming dilution factor of 4 is used for unknown samples.

Component	Conc. range (wt%)
Na ₂ O	0.32–5.10
MgO	0.33–5.73
Al ₂ O ₃	0.08–21.26
SiO ₂	0.7–82.1
P ₂ O ₅	0.04–3.26
K ₂ O	0.08–2.39
CaO	0.84–57.32
TiO ₂	0.06–3.00
Fe ₂ O ₃	1.15–17.09
Mn	0.0215–0.3687
Sr	0.0038–0.12856

consists of fine grained sandstone, siltstone and bioclastic grainstone/packstone^[21] in which SiO₂ and CaO concentrations vary considerably. Therefore, a wide range of concentrations of these elements is necessary in a calibration. The RMs BCR-2 and COQ-1 were used as representative of silicate and carbonate matrices in the calibration.

Among sedimentary rocks, Green river shale (SGR-1) and Bush creek shale (SBC-1) were analyzed to evaluate the method. Further, a metamorphic rock, Mica Schist (SDC-1), and variety of igneous rocks including Granodiorite (GSP-2), Andesite (AGV-2), Basalt (BCR-2), Diabase (W-2), Quartz latite (QLO-1) and Carbonatite (COQ-1) were also analyzed. These RMs provided a reasonably dynamic range of elemental compositions to validate the moderate or extreme concentrations in calibration application. For example COQ-1 contains sufficiently high CaO concentration and low concentration of SiO₂, Al₂O₃, and K₂O, whereas GSP-2 contains low amount of CaO, MgO but high concentrations of SiO₂ and K₂O.

Sample preparation

The USGS RMs used in this study are BCR-2, AGV-2, COQ-1, GSP-2, NOD-A-1, and SBC-1. Pure Silica was purchased from Technical Glass products (TGP, purity > 99.99%) and Aluminum Oxide, XRF grade (LOT: A0302078, 99.99% purity) was purchased from Acros Organics.

The fusion bead method was used as fusion is a more reliable technique for measuring major constituents in geologic samples when compared with the pressed pellet technique. It provides enhanced homogeneity, reduces matrix effects, and eliminates mineralogical and particle size effects.^[17,20] Initially, the powder samples of BCR-2 and COQ-1 were analyzed by a Laser Diffraction Particle Size Distribution analyzer (LD-PSD, Beckman Coulter LS 13 320) to measure the particle size distribution of each RM powder (Fig. 1). Results in Table 1 show that 90% of BCR-2 particles are smaller than 54 μm, with mean value of 25.61 μm. For COQ-1, 90% of particles are below 60 μm, with mean value of 19.74 μm. Particle size of a specimen is an important parameter to consider when trying to obtain a homogenized glass bead as large particles (generally above 100 μm) are difficult to dissolve in flux and therefore require harsher conditions (e.g. higher temperature or additional time) to dissolve.^[15] Proper fusion conditions ensure an absence of cloudiness in a bead (as cloudiness represents more dispersion rather than dissolution). Dispersed compositions within a bead increase heterogeneity and matrix effects that may compromise the accuracy of results.

A total of 13 glass beads were prepared from pre-dried (at 110°C), sub-sampled (riffle splitter) BCR-2 and COQ-1 using variable sample to flux ratios. Oven-dried samples were stored in a desiccator to avoid moisture absorption. Accurately weighed (±0.1 mg) samples and dilithium tetraborate (Li₂B₄O₇) flux were mixed in a plastic jar by using a touch mixer, transferred to pre-conditioned graphite crucibles, and fused in a muffle furnace for 20 min at 1100°C. The crucibles were taken out, allowed to cool and fused for an extra 20 min at 1100°C to avoid heterogeneity, inclusions, or cracking that may form in the first round of fusion.^[15,22] The oven was shaken at a certain time for 10 min when the mixture is molten to provide sufficient kinetic energy to obtain maximum diffusion of the specimen within the flux. Transparent beads were polished and washed with alcohol in an ultrasonic bath for 30 s to remove any residue, which may have been introduced. Beads were ensured to be sufficiently thick (infinite thickness) for the X-ray measurements

by XRF software (ZSX (Rigaku, The Woodlands, Texas, USA): Analytical Evaluation), where the analytical errors can be identified by software based on the actual inputs.

Arbitrary initial sample and flux masses were used such that the total mass of each bead is between 11–14g, however, the exact numbers for the dilution factors were calculated and input into the calibration application. For BCR-2 the following dilution factors were obtained: 3, 4, 6, 10, 12, 21, and 54. For COQ-1 the dilution factors are as follows: 3, 4, 6, 10, and 24 (Table 2).

The same method was used to fuse SGR-1, SDC-1, QLO-1, W-2, AGV-2, SBC-1, and GSP-2, with dilution factor 4. AGV-2 and GSP-2 with dilution factor 2, and SDC-1 and QLO-1 with dilution factor 9 were also prepared for further study. In addition, three synthetic fusion beads were prepared from pure components of SiO₂ and Al₂O₃ including ARG-1, ARG-2, and Pure-Si. These beads in addition to BCR-2 and COQ-1 beads were used to examine the reliability of the calibration method. For this purpose all the RMs were run five times alternately (to avoid overheating the beads exposed to X-ray beam) to measure the uncertainty related to the reproducibility.

Calibration plots

A Wavelength-Dispersive X-ray Fluorescence instrument was used in this study. The Rigaku Supermini 200 is a benchtop model with a Palladium target; instrument conditions were 50kV and 4mA, which were constant throughout this study. Only the major and minor constituents of usual geologic specimens were targeted for this application (Na, Mg, Al, Si, P, K, Ca, and Fe).^[10] Because of the extreme dilution technique (up to 52 times), no attempt was made to detect trace elements at the µg/g level, as sensitivity decreases dramatically at such high dilution. Among the trace elements only Sr and Mn were included as their concentrations in the RM samples (BCR-2, COQ-1) were considerable. Table 3 represents the measuring conditions and overlap corrections for each element. The overlaps in measured intensities were corrected by using the overlap correction coefficients.

To perform this set of experiments, the XRF software package utilized should be capable of dilution variation as the input values of each CRM (BCR-2 and COQ-1) are constant throughout and only the dilution factors change from sample to sample. The software package used in this study is ZSX (version 7.41 MPU 1.002 contains Fusion Disk Correction).

In XRF analysis, measured intensities are calculated against the concentration for each element. By using the FP method, the concentration of each element is converted to the theoretical intensity and then the theoretical intensities are used to calculate the matrix correction coefficients.^[23] Calculated theoretical intensities are plotted against net measured intensity of each element to develop the calibration plot.

The influence of coexisting elements was calculated by the software program. ZSX software has an automatic correction program that calculates the alpha coefficients based on the best algorithm matched with the RM composition. The auto correction was chosen for this application. Matrix coefficients are subject to change with alteration in dilution factor; however, we were uncertain whether this difference is trivial or substantial in practice. Kimura and Yamada^[13] have shown that the difference in the matrix coefficients at dilution factors of 5 and 2 is insignificant. For this application matrix coefficients are calculated with dilution factor of 4.

Both BCR-2 and COQ-1 were used to establish calibration lines to measure the major and minor elements present in most of the rock

Table 5. Results obtained for USGS reference materials.

Component	SGR-1		SDC-1		QLO-1		W-2	
	Avg. V.	R.V.	Avg. V.	R.V.	Avg. V.	R.V.	Avg. V.	R.V.
Na ₂ O (%)	2.95±0.01	2.99±0.07	2.01±0.02	2.05±0.05	4.09±0.04	4.2±0.07	2.13±0.04	2.20±0.02
MgO (%)	4.22±0.05	4.44±0.10	1.74±0.02	1.69±0.05	1.06±0.02	1.00±0.04	6.26±0.05	6.37±0.03
Al ₂ O ₃ (%)	6.45±0.05	6.52±0.11	15.81±0.05	15.8±0.17	16.14±0.09	16.2±0.10	15.51±0.06	15.45±0.08
SiO ₂ (%)	27.9±0.12	28.2±0.11	66.0±0.1	65.8±0.2	65.9±0.1	65.6±0.2	52.7±0.1	52.7±0.2
P ₂ O ₅ (%)	0.26±0.02	0.328±0.03	0.17±0.01	0.16±0.13	0.28±0.01	0.25±0.01	0.08±0.01	0.14±0.06
K ₂ O (%)	1.58±0.02	1.66±0.05	3.25±0.02	3.28±0.05	3.62±0.02	3.6±0.06	0.6±0.03	0.63±0.01
CaO (%)	8.08±0.12	8.38±0.09	1.31±0.07	1.4±0.04	3.06±0.05	3.17±0.04	10.82±0.05	10.86±0.04
TiO ₂ (%)	0.27±0.01	0.253±0.01	0.99±0.01	1.01±0.02	0.63±0.01	0.62±0.02	1.07±0.01	1.06±0.01
Fe ₂ O ₃ (%)	2.86±0.05	3.03±0.07	6.85±0.05	6.99±0.11	4.31±0.04	4.35±0.07	10.91±0.04	10.83±0.11
Mn (µg/g)	252±7	267±17	864±10	880±30	—	—	1285±11	1293±20
Sr (µg/g)	392±6	418±6	167±7	180±5	331±6	340±6	177±6	190±2

Avg. V., average value accompanied by uncertainty; R.V., reference value; USGS, US Geological Survey.

samples. BCR-2 has a relatively high concentration of SiO₂, Al₂O₃, and Fe₂O₃, whereas COQ-1 contains a high concentration of CaO (Fig. 2). The combination of these two RMs allows for a wide range

of concentrations in the calibration that is mainly suitable for silicate and carbonate rich and/or other compositions between these spectra. Minimum and maximum data points for each calibration

Table 6. Results obtained for USGS reference materials.

Component	AGV-2		SBC-1		GSP-2	
	Avg. V.	R.V.	Avg. V.	R.V.	Avg. V.	R.V.
Na ₂ O (%)	4.21±0.05	4.19±0.07	—	<0.15	2.68±0.04	2.78±0.05
MgO (%)	1.82±0.02	1.79±0.02	2.59±0.02	2.6±0.01	0.99±0.02	0.96±0.02
Al ₂ O ₃ (%)	17.05±0.09	16.91±0.11	20.56±0.04	21±0.14	14.80±0.04	14.9±0.10
SiO ₂ (%)	59.6±0.1	59.3±0.35	46.9±0.2	47.6±0.2	66.1±0.1	66.6±0.4
P ₂ O ₅ (%)	0.47±0.01	0.48±0.01	0.39±0.01	0.37±0.01	0.31±0.01	0.29±0.01
K ₂ O (%)	2.94±0.02	2.88±0.06	3.42±0.02	3.45±0.01	5.41±0.02	5.38±0.07
CaO (%)	5.08±0.04	5.2±0.07	2.86±0.05	2.95±0.01	1.99±0.05	2.1±0.03
TiO ₂ (%)	1.06±0.01	1.05±0.11	0.84±0.01	0.86±0.01	0.69±0.02	0.66±0.01
Fe ₂ O ₃ (%)	6.81±0.06	6.69±0.05	9.77±0.02	9.71±0.02	4.84±0.04	4.9±0.08
Mn (μg/g)	776±7	770±10	1143±9	1162±8	297±11	320±10
Sr (μg/g)	661±6	658±9	167±6	178±1	228±9	240±5

Avg. V., average value accompanied by uncertainty; R.V., reference value; USGS, US Geological Survey.

Table 7. Results obtained for USGS reference materials.

Component	BCR-2				COQ-1			
	Avg. V.	R.V.	Δm	UΔ	Avg. V.	R.V.	Δm	UΔ
Na ₂ O (%)	3.2±0.05	3.16±0.06	0.04	0.15	—	<0.1	—	—
MgO (%)	3.53±0.07	3.59±0.03	0.06	0.16	1.2±0.02	1.25	0.05	0.06
Al ₂ O ₃ (%)	13.6±0.04	13.5±0.10	0.1	0.21	0.42±0.02	0.37±0.02	0.05	0.06
SiO ₂ (%)	54.1±0.1	54.1±0.4	0	0.8	3.5±0.1	3.5±0.1	0	0.3
P ₂ O ₅ (%)	0.36±0.04	0.35±0.01	0.01	0.08	2.7±0.04	2.6±0.06	0.1	0.14
K ₂ O (%)	1.77±0.02	1.79±0.03	0.02	0.07	0.18±0.02	0.16±0.01	0.02	0.05
CaO (%)	7±0.04	7.12±0.06	0.12	0.13	48.35±0.10	48.3±0.19	0.05	0.43
TiO ₂ (%)	2.23±0.02	2.26±0.03	0.03	0.07	0.21±0.04	0.15±0.001	0.06	0.07
Fe ₂ O ₃ (%)	13.94±0.02	13.8±0.10	0.14	0.22	3.00±0.02	2.94±0.05	0.06	0.10
Mn (μg/g)	1514±10	1520±30	6	63	3328±26	3330±8	2	55
Sr (μg/g)	328±7	346±7	18	20	12047±14	12000±50	47	103

Avg. V., average value accompanied by uncertainty; R.V., reference value; USGS, US Geological Survey; Δm, difference between average and reference value; UΔ, expanded uncertainty.

Table 8. Comparison of expanded uncertainty (UΔ) with difference between average and reference value (Δm).

Analyte	SGR-1		SDC-1		QLO-1		W-2		AGV-2		SBC-1		GSP-2	
	Δm	UΔ	Δm	UΔ	Δm	UΔ	Δm	UΔ	Δm	UΔ	Δm	UΔ	Δm	UΔ
Na ₂ O (%)	0.04	0.13	0.04	0.10	0.11	0.15	0.07	0.08	0.02	0.16	—	—	0.10	0.12
MgO (%)	0.22	0.22	0.05	0.11	0.06	0.09	0.11	0.12	0.03	0.06	0.01	0.05	0.03	0.06
Al ₂ O ₃ (%)	0.07	0.23	0.01	0.35	0.06	0.26	0.06	0.20	0.14	0.27	0.44	0.29	0.1	0.21
SiO ₂ (%)	0.3	0.3	0.2	0.5	0.3	0.5	0	0.5	0.3	0.7	0.7	0.7	0.5	0.8
P ₂ O ₅ (%)	0.07	0.08	0.01	0.04	0.03	0.03	0.06	0.12	0.01	0.03	0.02	0.03	0.02	0.03
K ₂ O (%)	0.08	0.11	0.03	0.11	0.02	0.13	0.03	0.05	0.06	0.12	0.03	0.05	0.03	0.15
CaO (%)	0.30	0.30	0.09	0.16	0.11	0.13	0.04	0.13	0.12	0.15	0.09	0.10	0.11	0.12
TiO ₂ (%)	0.02	0.04	0.02	0.05	0.01	0.04	0.01	0.03	0.01	0.22	0.02	0.03	0.03	0.05
Fe ₂ O ₃ (%)	0.17	0.17	0.14	0.25	0.04	0.16	0.08	0.23	0.12	0.16	0.06	0.06	0.06	0.18
Mn (μg/g)	15	37	16	63	—	—	8	46	6	25	19	24	23	30
Sr (μg/g)	26	32	13	17	9	17	13	13	3	21	11	12	12	20

Table 9. The analyses results of three synthetic beads made of SiO₂ and Al₂O₃.

Component	ARG-1 (n=10)		ARG-2 (n=3)		Pure SiO ₂ (n=3)	
	Avg. V.	R.V.	Avg. V.	R.V.	Avg. V.	R.V.
Al ₂ O ₃ (%)	20.19±0.06 ^a	20	30.23±0.05	30	—	—
SiO ₂ (%)	79.9±0.2	80	69.7±0.1	70	98.9±0.1*	99.9

*Extrapolated data; n: number of runs.
Avg.V., average value accompanied by standard deviation; n: number of runs; R.V., reference value.

line can be estimated for each element by assuming that a dilution factor of 4 will be used for unknown samples. We used experimental intensity (kcps) of each element at a dilution factor of 4 to obtain the normalized intensity per mass unit (sensitivity) coefficient (kcps/(mass %)). Subsequently, to obtain the corresponding mass % of each element for each RM at both the lowest and highest dilution factor, we divided the experimental intensity of each element by the obtained coefficients. The upper and lower limits of the calibration line are defined by the lowest and highest dilution factor, respectively.

For example, Si in BCR-2 (the most Si-rich sample with SiO₂ concentration 54.1%) at dilution factor of 4 has a measured intensity of 21.3kcps. Normalizing the measured intensity per mass unit results in (0.394) kcps/(mass %) for Si. This number can be used to calculate the limit range assuming that the dilution factor is 4.

For upper limit (BCR-2, Dilution Factor: 2), the experimental value is 32.3kcps. Using the coefficients calculated above result in 82% concentration for silica. Using the theoretical intensity for the same RM, results almost the same value (83%).

In order to evaluate the defined limit range, we analyzed a synthetic bead (ARG-1: 80% SiO₂ and 20% Al₂O₃ concentrations) against the Si calibration line. As Fig. 3 shows, the data point for SiO₂ falls on the line close to the BCR-2 at dilution factor 2, which validates the limit range calculation. Note that because of the applied FP corrections the exact prediction of the limit with this method is difficult. We recommend that an even narrower range be defined to ensure the results are within the calibration line limits to ensure no extrapolation is practiced. Analysis of ARG-1 provided

a precise and accurate result of 79.9±0.2% (average±standard deviation) for SiO₂. Hence, the upper and lower limits of calibration lines were calculated for all elements using experimental intensities using the above mentioned method (Table 4). These data will be explained in the results and discussion section.

Results and discussion

We have established that it is practical to create a calibration method using the least number of RMs and using variation in flux-to-substance ratios. Correlation coefficient values (R²) greater than 0.999 were obtained for all the elements. This approach provides a feasible method to choose the most suitable RM(s) in terms of matrix similarity to the real specimen (e.g. elemental compositions, volatility of constituents (Sulphur, etc.), particle size distribution, and loss on ignition). In addition, this method provides a much larger range of concentrations for each element with only two RMs. For instance, the SiO₂ calibration line theoretically covers a wider range of 0.7–82% in this application, whereas the used values of SiO₂ in the RM (COQ-1 and BCR-2) are 3.47 and 54.1%.

To validate the calibration application seven independent RMs in addition to BCR-2, COQ-1 (Dilution Factor: 4) were analyzed. As explained in the introduction these nine RMs represent a variety of matrices e.g. igneous, metamorphic, and sedimentary rocks. Tables 5–7 present the average values and reference values with their related uncertainties for USGS RMs. Uncertainties of the reference values were calculated as recommended in literature.^[24–26] Tables 7 and 8 summarize the comparison of absolute difference between mean average values and reference values with the expanded uncertainty. The expanded uncertainty is calculated by using a coverage factor (k) of 2, which represents a level of confidence of approximately 95%. When the measured difference (Δm) is equal to or smaller than the expanded uncertainty (UΔ), the difference between average and reference values is considered insignificant. All the results show a good agreement between Δm and UΔ. All of the Δm values are equal to or smaller than UΔ.

One additional way to validate the calibration method is to fuse and examine pure chemicals. Although the matrix here is inherently simpler than the matrix of natural geologic specimens, the examination can provide insightful data regarding where anomalies may occur. It specially can be useful when the extreme

Table 10. Results obtained for USGS reference materials with 1:2 sample-to-flux ratio.

Analyte	GSP-2				AGV-2			
	Avg. V.	R.V.	Δm	UΔ	Avg. V.	R.V.	Δm	UΔ
Na ₂ O (%)	2.81±0.02	2.78±0.05	0.03	0.10	4.03±0.05	4.19±0.07	0.16	0.16
MgO (%)	1.00±0.02	0.96±0.02	0.04	0.06	1.78±0.02	1.79±0.02	0.01	0.06
Al ₂ O ₃ (%)	14.7±0.04	14.9±0.10	−0.20	0.21	16.96±0.02	16.91±0.11	0.05	0.22
SiO ₂ (%)	65.7±0.2	66.6±0.4	−0.9	0.9	59.1±0.1	59.3±0.35	0.2	0.7
P ₂ O ₅ (%)	0.28±0.01	0.29±0.01	−0.01	0.03	0.50±0.01	0.48±0.01	0.02	0.03
K ₂ O (%)	5.43±0.02	5.38±0.07	0.05	0.15	2.85±0.02	2.88±0.06	0.03	0.12
CaO (%)	2.01±0.04	2.1±0.03	−0.09	0.10	5.05±0.05	5.2±0.07	0.15	0.16
TiO ₂ (%)	0.67±0.01	0.66±0.01	0.01	0.03	1.02±0.01	1.05±0.11	0.03	0.22
Fe ₂ O ₃ (%)	5.07±0.04	4.9±0.08	0.17	0.18	6.56±0.06	6.69±0.05	0.13	0.16
Mn (μg/g)	306±9	320±10	−14	26	744±14	770±10	26	34
Sr (μg/g)	233±6	240±5	−7	16	638±6	658±9	20	21

Avg. V., average value accompanied by uncertainty; R.V., reference value; USGS, US Geological Survey; Δm, difference between average and reference value; UΔ, expanded uncertainty.

Table 11. Results obtained for USGS reference materials with 1 : 9 sample-to-flux ratio.

Analyte	SDC-1				QLO-1			
	Avg. V.	R.V.	Δm	$U\Delta$	Avg. V.	R.V.	Δm	$U\Delta$
Na ₂ O (%)	1.94±0.04	2.05±0.05	0.11	0.12	4.07±0.04	4.2±0.07	0.13	0.15
MgO (%)	1.73±0.02	1.69±0.05	0.04	0.11	1.07±0.02	1.00±0.04	0.07	0.09
Al ₂ O ₃ (%)	15.81±0.07	15.8±0.17	0.02	0.37	16.19±0.14	16.2±0.10	0.01	0.33
SiO ₂ (%)	66.0±0.1	65.8±0.2	0.3	0.5	66.0±0.1	65.6±0.2	0.4	0.5
P ₂ O ₅ (%)	0.17±0.01	0.16±0.13	0.02	0.04	0.30±0.02	0.25±0.01	0.05	0.05
K ₂ O (%)	3.25±0.020.04	3.28±0.05	0.01	0.12	3.61±0.05	3.6±0.06	0.01	0.16
CaO (%)	1.31±0.07	1.4±0.04	0.16	0.16	3.03±0.06	3.17±0.04	0.14	0.15
TiO ₂ (%)	0.99±0.01	1.01±0.02	0.03	0.05	0.65±0.01	0.62±0.02	0.03	0.04
Fe ₂ O ₃ (%)	6.85±0.05	6.99±0.11	0.07	0.25	4.30±0.04	4.35±0.07	0.05	0.15
Mn (µg/g)	864±10	880±30	14	67	—	—	—	—
Sr (µg/g)	167±7	180±5	14	20	326±5	340±6	14	17

Avg. V., average value accompanied by uncertainty; R.V., reference value; USGS, US Geological Survey; Δm , difference between average and reference value; $U\Delta$, expanded uncertainty.

concentrations of elements are required. Two synthetic beads (ARG-1 and ARG-2; SiO₂ : Al₂O₃ 80:20% and 70:30% respectively) were analyzed. As shown in Table 9 the results were highly accurate even though Al₂O₃ has been extrapolated in the case of ARG-2. In addition, a pure silica bead was analyzed to examine the linearity of the calibration line for SiO₂; the percent error is only 1.3% (average value of 98.9±0.1 vs reference value of 99.9) allowing for reliable extrapolation where necessary Table 10 and 11.

Another advantage of such an application is the flexibility of dilution factor over a wide range of concentrations and in such a case the specimen is not restricted to a constant amount of sample or dilution ratio. This is an important factor when the solubility of a sample is low in a given flux. In such a case, excessive dilution can be employed to resolve solubility issues. Further, low dilution may be beneficial as well. When the sensitivity of an instrument for an element of interest is insufficient, low dilution (e.g. 2:1 flux-to-sample ratio) can help to detect the element with higher confidence. To verify such an assumption GSP-2 and AGV-2 at 1:2 dilution and SDC-1 and QLO-1 at 1:9 dilution were examined, and all the data were acceptable because measured difference values (Δm) are equal to or smaller than expanded uncertainty values ($U\Delta$), and therefore, the difference between average and reference values is considered insignificant. However, under normal circumstances, we would recommend the dilution factor for unknown samples to be in the moderate dilution range (3–6 times dilution) as this will decrease the chance of deviation associated with sample preparation^[15] and limit range definition, which was explained previously.

Conclusion

We have introduced a simple yet effective method to establish a quantitative calibration application with the least number of RMs. Evaluation of the calibration curves against the independent RMs and synthetic fusion beads shows excellent conformance. Validation of the entire set of RMs shows the reliability of the method that results from the quality of homogenous beads, smooth surface of beads, stability of the instrument and optimal setting parameters of calibration (background definition, peak maximum, scan time, etc.). In addition, this technique provides a dynamic range of dilution, so the dilution is not limited to a single factor and can be adjusted depending on the requirement of the nature of each sample.

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References

- [1] K. Tani, H. Kawabata, Q. Chang, K. Sato, Y. Tatsumi. *Front Res Earth Evol* **2005**, 2, 1.
- [2] F. Demir, G. Budak, E. Baydaş, Y. Şahin. *Nucl Instrum Methods Phys Res, Sect B* **2006**, 243, 423.
- [3] Z. Mzyk, I. Baranowska, J. Mzyk, X. Ray. *Spectrom* **2002**, 31, 39.
- [4] S. West, D. Charman, J. Grattan, A. Cherburkin. *Water Air Soil Pollut* **1997**, 100, 343.
- [5] F. Melquiades, C. J. Appoloni. *Radioanal Nucl Chem* **2004**, 262, 533.
- [6] X. Bi, P. Wang, H. Jiang. *J Hazard Mater* **2008**, 154, 543.
- [7] J. Jurczyk, R. Sitko, B. Zawisza, F. Buhl, E. Malicka. *Microchim Acta* **1999**, 132, 41.
- [8] R. Klockenkämper. *Spectrochim Acta Part B* **2006**, 61, 1082.
- [9] M. Pouzar, T. Černohorský, A. Krejčová. *Talanta* **2001**, 54, 829.
- [10] A. Blank, L. Eksperianova, X. Ray. *Spectrom* **1998**, 27, 147.
- [11] J. Hutton, S. Elliott. *Chem Geol* **1980**, 29, 1.
- [12] R. Lee, D. McConchie, X. Ray. *Spectrom* **1982**, 11, 55.
- [13] Y. Y. JJun-ichi Kimura. *Petrol Mineral Econ Geol* **1996**, 91, 62.
- [14] D. Johnson, P. Hooper, R. Conrey. *Adv X-Ray Anal* **1999**, 41, 843.
- [15] K. Nakayama, T. Nakamura. *Anal Sci* **2005**, 21, 815.
- [16] K. Kataoka. *Rigaku J* **1989**, 6, 33.
- [17] K. Nakayama, T. Nakamura, X. Ray. *Spectrom* **2008**, 37, 204.
- [18] R. Rousseau. *J Geosci Geom* **2013**, 1, 1.
- [19] H. Kodama, J. Brydon, B. Stone. *Geochim Cosmochim Acta* **1967**, 31, 649.
- [20] P. E. Mori, S. Reeves, C. T. Correia, M. Haukka. *Brazilian J Geol* **1999**, 29, 441.
- [21] J. P. Zonneveld, T. W. Breatty, R. B. MacNaughton, S. G. Pemberton, J. Utting, C. M. Henderson. *Can Petrol Geol* **2010**, 58, 115.
- [22] V. Karmanov, V. Zagorodny. *Adv X-Ray Anal* **1991**, 35, 749.
- [23] K. Kansai. *Rigaku J* **2008**, 24, 4.
- [24] T. Linsinger. Comparison of a measurement result with the certified value, European Communities: Geel, **2005**, http://www.erm-crm.org/ERM_products/application_notes/application_note_1/Documents/erm_application_note_1_english_rev3.pdf. Accessed on 13/8/16.
- [25] J. S. Kane, P. J. Potts. *Geostand Geoanal Res* **2007**, 31(4), 361.
- [26] M. F. Gazulla, M. Rodrigo, S. Vicente, M. Ordu na. *X-Ray Spectrom* **2010**, 39, 321.