Technical Note

Special tablets containing cellulose binder and Sr internal standard for simplifying X-ray fluorescence analysis of powder samples

Zofia Mzyk *, Jacek Anyszkiewicz, Tadeusz Gorewoda

Institute of Non-Ferrous Metals, Sowinskiego 5, 44-100 Gliwice, Poland

ARTICLE INFO

ABSTRACT

The addition of a constant amount of $SrCO_3$ was observed to be the proper internal standard for analysis by wavelength-dispersive X-ray fluorescence spectrometry to correct the matrix and grain size effects of many constituents. The weighing of constant amounts of $SrCO_3$, binder and sample allowed for the preparation time for analysis to be extended, and special tablets containing binder and $SrCO_3$ were developed. Several substances were tested as binders, among which microcrystalline cellulose was chosen for further study. The prepared tablets were checked for their weight stability and the repeatability of $SrCO_3$ addition. The tablets were then used to prepare pellets from geological samples for X-ray fluorescence analysis. The exemplary application and calibration curves for several analytes confirmed that the prepared tablets could be useful for the pelletizing of such materials to compensate for matrix effects.

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1. Introduction

The internal standard (IS) method is widely used in analytical chemistry. The method is particularly simple to apply for liquid sample analysis. A correctly selected IS could be added in a well-measured quantity by micropipetting for example. For that reason, there are many examples of the application of an IS in wet analytical methods.

The fundamental principle of this method in chemical analysis as well as in X-ray fluorescence spectrometry (XRF) analysis is based on the addition of a known amount of one or more elements, which is used as the IS, to all blanks, calibration solutions, and samples [1,2]. For elements affected by changes in experimental conditions, the use of the ratio of the analyte signal intensity to the IS signal intensity might compensate for variations [3].

For heterogeneous samples, the application of an IS to compensate for errors due to difficult sampling has also been studied. For example, nickel was used as an IS to determine Pb, Ti, Zr, Bi, Nb and Mn by using the XRF thin layer method [4].

The IS method has also been used in XRF analytical methods. In total reflection XRF (TXRF), to compensate for errors due to difficult sampling and matrix effects, gallium has been used as an IS [5]. However, IS in TXRF is also used as a quantification mode (external calibration is not needed). Moreover, strontium has been used as an IS for dissolved samples of alloys, analyzed as a thin layer, to compensate for the complicated preparation procedures of dissolving, micropipetting and drying on staked filter media [3]. Similarly, Zawisza et al. reported the use of cobalt as an IS for the determination of Te, Bi, Ni, Sb and Au in anode slime [6].

These examples pertain to liquid samples. In our previous studies, a weighed amount of $SrCO_3$ was added to powdered samples of slags or geological samples [7]. We observed that such an addition was useful for matrix effect and particle size effect corrections. The particle size corrections were achieved by the filling of space among grains, where a large amount of IS filled large spaces such that the measured intensity of Sr was high. The Sr-Lα line was especially sensitive to grain size because the measured depth was comparable to the particle size. The usefulness of such an addition was proven by using a sample preparation procedure with the addition of 0.5000 g of $SrCO_3$ for copper concentrates, slags from metallurgical copper processes, and alloys in the form of chips milled with an abrasive [8]. Strontium has two easily measured fluorescent lines, Kα and Lα. These lines reflect the total matrix effect (Sr-Kα) and particle size effect (Sr-Lα); therefore, their intensities could be used to calculate the empirical coefficients. Strontium as an IS was also applied by Li et al. to improve the precision and accuracy of Cu in copper ore [9], and by Shalin and Magnusson to enable analysis of 77 elements in inhomogeneous solid waste samples of a various matrix [10]. Another application of this method is in determining the proper grinding time (as suggested in the handbook [1]) required to reach a constant value of Kα/Lα. In an industrial analytical laboratory, where hundreds of pellets are prepared, measurements of these lines in systematically prepared specimens of the same material could provide information about the wear of equipment, especially mills.

The addition of an IS, as a weighed portion, complicates analytical procedures and extends the duration thereof, especially in comparison to the time required for simple pelletizing. Adopting such a procedure in an industrial laboratory could be problematic or even impossible. To simplify the pellet preparation procedure for XRF analysis, we developed specially prepared tablets containing binder and $SrCO_3$.

* Corresponding author. Tel.: +48 322380368.
E-mail address: zofia.mzyk@imn.gliwice.pl (Z. Mzyk).

2. Experimental

2.1. Instrumentation

For the homogenization of the binder and 10% $SrCO_3$, a V-mixer with steel balls made by Testchem was used. An experimental series of tablets was created using a ZP19 rotary tablet machine (Shanghai Tianfeng Pharmaceutical Machinery Co.).

All XRF measurements were performed with a ZSX Primus X-ray fluorescence spectrometer (Rigaku) equipped with a 4 kW Rh tube, scintillation and flow proportional counters, five primary beam filters (Be, Zr, Cu, Ti and Al), six diaphragms (masks) allowing to analyze samples of various diameters (35 mm, 30 mm, 20 mm, 10 mm, 1 mm, 0.5 mm), seven crystals (LiF200, LiF220, germanium, pentaerythritol, and three multilayers: RX25, RX35, RX61). The measurement chamber was under vacuum condition. In this study, a new XRF application was developed with measurement parameters as in Table 1. The following equipment was necessary for milling and pelletizing the powder samples: a vibrating grinder LMW model made by Testchem (Poland) and a HTP40 hydraulic press made by Herzog (maximum pressure 26 kN/cm^2).

2.2. Examination of several binders for preparing binder and IS mixtures

As binders that are commonly used, wax, cellulose and boric acid (Avantor Performance Materials, Poland, all of lab. purity grade) were tested for their ability to yield homogeneous mixtures with 10% strontium carbonate (Avantor Performance Materials, Poland, lab. purity grade). The initial experiments involving wax resulted in the rejection of the binder because it was impossible to obtain a homogeneous mixture with $SrCO_3$. Moreover, cellulose and boric acid were observed to be prospective binders. The following experiments with the tablet machine showed that the use of boric acid makes consistent tableting difficult. Tablets obtained from the boric acid mixture had no consistent mass, likely caused by the binder's strong electrostatic properties, which resulted in contamination of the tablet machine stamps. The most convenient binder was determined to be cellulose mixed with $SrCO_3$ (10%), magnesium stearate (1%) and silicone dioxide (0.5%, aerosil). The additives served as lubricants for tableting.

2.3. Examination of the consistency of prepared tablets

The obtained test charge of the tablets was checked for consistency in the mass of the tablets and the amount of $SrCO_3$ added. To test for a consistent mass, three sets of 30 tablets from three jars were weighed individually. The calculated standard deviation for the mass of a single tablet when the average mass was equal to 0.290 g was 0.003 g (1% relative standard deviation). To check for the consistent addition of $SrCO_3$, five pellets were prepared from each of four tablets, and the Sr-Kα line was measured (50 kV, 60 mA with Zr primary beam filter, registered

with a scintillation detector). The calculated relative standard deviation for the registered Sr-Kα intensity was 0.37%.

2.4. Examination of the usability of the prepared tablets as an IS and binder

Tablets were used to prepare pellets for XRF measurements. The addition of a typical pure binder in this form is popular in XRF specimen preparation. Three grams of analytical sample and three tablets with IS were ground for 3 min in a vibrating grinder using a stainless steel bowl and puck. In this manner, we prepared three materials with various sensitivities for pelletizing, copper concentrate, copper ore and slag from copper metallurgy. After the powdered mixture was pressed, the pellets were checked for resistance to the conditions of normal use and X-ray radiation exposure. All pellets were stable and showed the expected appearance after being used several times.

To verify the usefulness of the tablets as an IS and to prove that a consistent amount of $SrCO_3$ was added to every tablet, the test charge of the tablets was used to prepare a calibration pellet series using geological materials obtained from copper ores mines. Composition of reference materials used for XRF application preparation is presented in Table S1 (Appendix A). Pellets were prepared as previously described. The obtained pellets were also time stable. The pellets were measured using the analytical program presented in Table 1.

For this study, homemade standards were used (geological materials: dolomite, sandstone and slate—from the Institute of Non-Ferrous Metals 2014). Different milling times were used to simulate grain size effect. Three pellets were prepared from each material using 2, 3 and 4 min of milling. Applying Sr intensities as the IS or for the empirically calculated coefficient gave a positive effect of better accuracy for eight of the thirteen analyzed elements. As an example, Table 2 shows the results obtained for sandstone. The results for dolomite and slate are collected in Table S2 (Appendix A).

3. Results and discussion

Positive effects of decrease in RSDs (residual standard deviations) were observed when the intensity of Sr-Kα was used as an IS for calibration curves of the following elements: Ag, Mo, Pb, As and (to a small degree) Cu. The most visible effect was observed for Pb, which is shown in Fig. 1.

Similar positive effects could be observed for the calibration curve of Ag, as shown in Fig. 2.

The materials used to examine the prepared test charge of the tablets were obtained from Polish copper mines and included sandstones, dolomites and shales. Their matrices varied, and several components showed a wide range of concentrations. The obtained RSDs are compared in Table S3 (Appendix A).

Analysis of the presented calibration curves demonstrates that the use of an IS in form of developed tablets could be helpful. It is possible to obtain a good correlation factor and good fitted standard points for a calibration curve in a few steps for various elements with fluorescent lines near the IS lines, such as Pb and Ag. Moreover, it is possible to use the intensities of the two lines of this IS to calculate the empirical correction coefficient for grain size for other elements. The Sr-Lα line is especially sensitive to grain size. The results presented in Table 2 and Table S2 (Appendix A) show that being able to apply intensities of Sr lines as an IS or being able to calculate empirical correction coefficients could improve precision for various elements. This also applies for samples affected with the grain size effect.

It must be admitted that, theoretically, the Sr-Kα line is not an appropriate IS line for the Pb-Lβ line or the Ag-Kα line. When Pb-Lβ is measured, the Sr-Kα line should not be used as an IS (because of different series), according to rules in handbooks [1,2]. Between the Ag-Kα line and the IS line there are strong lines emitted by the rhodium tube, which is against the rules of IS selection. Nevertheless, the observed improvement in the RSD is substantial. This finding could be explained by

Table 1
Parameters of XRF application for geological materials analysis.

Element line	kV–mA	Filter	Crystal	Angle (deg)	Background angle (deg)	Time (s)
Ag-Kα	60–60	Zr	LiF200	16.000	17.000	10
Mo-Kα	60–60	Ti	LiF200	20.320	21.000	10
As-Kβ	50–70	None	LiF200	30.430	31.000	10
Pb-Lβ	50–60	None	LiF200	28.240	31.000	10
Cu-Kα	50–40	None	LiF200	45.010	43.000	10
Fe-Kα	50–50	None	LiF200	57.500	58.500	10
Ca-Kα	40–60	None	LiF200	113.120	Not used	10
Si-Kα	30–100	None	PET	109.050	Not used	10
Sr-Kα	50–60	Zr	LiF200	25.130	Not used	10
Sr-Lα	30–100	None	PET	103.310	105.000	10