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Direct Analysis of Metal Ions in Solutions with High Salt Concentrations by Total Reflection X-ray Fluorescence (TXRF)

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ABSTRACT: Total Reflection X-ray Fluorescence (TXRF) is becoming more and more popular for elemental analysis in academia and industry. However, simplification of the procedures for analyzing samples with complex compositions and residual matrix effects is still needed. In this work, the effect of an inorganic ($CaCl_2$) and an organic (tetraalkylphosphonium chloride) matrix on metals quantification by TXRF was investigated for liquid samples. The samples were spiked with up to 20 metals at concentrations ranging from 3 to 50 mg L^{-1} per element, including elements with spectral peaks near the peaks of the matrix elements or near the Raleigh and Compton scattering peaks of the X-ray source (molybdenum anode). The recovery rate (RR) and the relative standard deviation (RSD) were calculated to express the accuracy and the precision of the measured element concentrations. In samples with no matrix effects, good RRs are obtained regardless of the internal standard selected. However, in samples with moderate matrix content, the use of an optimum internal standard (OIS) at a concentration close to the one of the analyte significantly improved the quantitative analysis. In samples with high concentrations of inorganic ions, using a Triton™ X-100 aqueous solution to dilute the sample during the internal standardization resulted in better RRs and lower RSDs compared to using only water. In samples with a high concentration of organic material, pure ethanol gave slightly better results than when a Triton™ X-100–ethanol solution was used for dilution. Compared to previous methods reported in the literature, the new sample preparation method gave a better accuracy, precision and sensitivity for the elements tested. Sample dilution with an OIS and the surfactant Triton™ X-100 (inorganic media) or ethanol (organic media) is recommended for fast routine elemental determination in matrix containing samples, as it does not require special equipment, experimentally derived case-dependent mathematical corrections or physico-chemical removal of interfering elements.

Total Reflection X-Ray Fluorescence (TXRF) is a competitive analytical technique based on atomic spectroscopy and it is ideal for the determination of elemental concentrations in biological, medicine and environmental samples.[1-9] Since the introduction of the technique in 1971 by Yonead and Horiuchi,[10] and its extensive experimentation in the 1990s by Aiginger and Wobrauschek[11-15], by Knoth and Schwenkes,[16-20] and more recently by Klockenkämper and von Bohlen,[5,21-23] TXRF is becoming more and more popular. The main industrial application of TXRF is found in the microelectronics industry for the analysis of wafer surfaces where sample quantification is performed by comparison of new wafers with clean wafers and wafers intentionally contaminated with the elements of interest. On the other hand, the major research application of TXRF is for trace elemental analyses in low matrix aqueous samples, where sample quantification can be done by internal standardization in order to get an intensity that is independent of the particle size, thickness or glancing angle, since the concentration ratio of the analyte to the internal standard (IS) remains constant.[23]

Like other XRF spectrometry techniques, TXRF allows for a non-destructive routine quantitation of many elements over a wide range of concentrations. In these techniques, the sample is irradiated with X-rays and the photons with sufficient energy can be (partly) absorbed by atoms in the sample which consequently eject an electron. It is during the subsequent rearrangement of electrons that element-specific X-ray photons are emitted, i.e. the X-ray fluorescence (XRF). The device depicts the detected X-ray photons in a spectrum that represents the number of counts *vs.* the energy, and the elemental composition of the sample is estimated from the relative intensities of the peaks in the XRF spectrum, as this is characteristic for each individual atom in the sample. More specifically, total reflection of X-rays occurs when the X-rays pass from one medium (e.g. air) to another with higher refractive index (e.g. a flat quartz glass sample carrier), below a particular small angle of incidence, the *critical angle* (0.1° for Mo-Kα X-rays).[24]

The main distinctive over the other variants of XRF is that TXRF only requires micro amounts of sample for a full analysis, as the X-rays can efficiently excite the atoms because of the low sample penetration depth. At small thicknesses (*infinitely thin sample*),[25] the photoelectrons have a much higher chance to escape the sample without getting scattered, assuring that the major contribution of the emitted X-ray photons originates from the sample. This reduces the background in the spectral peaks and provides 1000 times lower detection limits than other XRF spectrometry techniques.[18] In addition to the small incident angle (minimum scattering) and the small X-ray penetration depth (lower background), another factor contributing to the lower detection limit of TXRF is the constructive interference of the incident and reflected ray, giving rise to X-ray standing waves. The *infinitely thin sample* at dried residues is crucial for not disturbing the conditions of total reflection, little modifying the standing waves field intensity and obtaining reliable results and little quantification problems under one of the most serious issues in X-ray spectrometric methods: the matrix effect.[5,21,26,27] This makes TXRF advantageous for the analysis of complex material mixtures and spectral interferences that cannot, or are difficult to, be measured by other techniques.[7,28,29]

Matrix effects occur whenever the analyte is in a medium with other elements which absorb or scatter X-rays emitted by the analyte or *vice versa*. Consequently, ion suppression (or less typically ion enhancement) of analyte's signal occurs, what leads to bias in the intensity of the spectral peaks and, thus, in the determined concentration of the analyte. Matrix effects are common in environmental, aqueous, organic or soil samples[30] which quite often contain heavy elements, highly X-ray absorbing matrices, large grains or low-volatile oil-like substances. As mentioned above, TXRF can to some extent overcome these effects, contrary to other XRF methods, thanks to the minimum scattering of the escaping x-rays by the *infinitely thin sample*. However, at high salt concentrations, problems appear in preparing the required *infinitely thin sample* for TXRF analysis. In these cases, sample pre-treatments such as selective precipitation and filtration are necessary to preferably separate and remove the interfering elements, and reduce the background, achieving a film thinner than the critical thickness.[22,31-33]

The objective of this paper is to provide a simple, efficient and fast procedure for researchers interested in using TXRF to quantify different samples with a high-salt matrix, including measurements of trace concentrations (1—5 mg L^{-1}). Thus, neither mathematical corrections nor pre-treatment steps, such as co-precipitation, pH adjustment, precipitation, filtration, washing and drying,[34] chelation or selective chromatographic adsorption and subsequent elution of the metal complexes,[35] are required. Furthermore, special attention is paid to the reproducibility of the results and broadening the applicability of the TXRF technique to a wider range of research contexts.

EXPERIMENTAL SECTION

Solutions purposely containing several of 20 representative metals (chromium, Cr; manganese Mn; cobalt, Co; gallium, Ga; strontium, Sr; lanthanum, La; cerium, Ce; praseodymium, Pr; neodymium, Nd; samarium, Sm; europium, Eu; gadolinium, Gd; terbium, Tb; dysprosium, Dy; holmium, Ho; erbium, Er; thulium, Tm; ytterbium, Yb; lutetium, Lu and yttrium, Y) were prepared for analysis in TXRF using ICP certified standard solutions of 1000 ± 10 mg L^{-1} (Chemlab, Zedelgem, Belgium). Solutions of $CaCl_2$ ($CaCl_2{\cdot}2H_2O$ Sigma–Aldrich, Diegem, Belgium), NH_4NO_3 (Sigma–Aldrich, Diegem, Belgium) and $C_{32}H_{68}ClP$ (trihexyl(tetradecyl)phosphonium chloride, commercial name Cyphos® IL 101, from Cytec Solvay Group, Canada), in ultrapure water or ethanol (absolute, VWR, Belgium) were used to vary the matrix presence in the metal solutions. The non-ionic surfactant alkylaryl polyether alcohol, commercially known as Triton™ X-100 (Sigma–Aldrich, Diegem, Belgium) was in specific cases employed during sample preparation.

The samples were measured on polished quartz glass disks, with a diameter of 30 mm and a thickness of 3 mm. The sample preparation

followed four steps: (1) hydrophobization; (2) internal standardization; (3) sample deposition; (4) gain correction.

Hydrophobization. To prevent the pipetted sample droplet from moving and spreading on the carrier, 30 µL of a silicone solution in isopropanol (SERVA® Electrophoresis GmbH, Heidelberg, Germany) was added on the carrier surface and dried for 20 min at 60 °C in a hot air oven.[36]

Internal standardization. The samples were prepared in 1.5 mL microtubes with standard solutions of 1000 mg L^{-1}. The samples had a final volume of 1 mL and contained between 3 and 20 metals with final concentrations from 3 to 50 mg L^{-1} of each element. The concentration of the internal standard (IS) used was in general equal to the concentration of the analyte(s).[37] Ultrapure water, ethanol or a solution of 53.5–107 g L^{-1} Triton™ X-100 was used to make a final volume of 1 mL. The solutions were homogeneously mixed on a vibrating plate (IKA MS 3 basic).

Sample deposition. A small droplet of the sample solution containing the analyte and IS was micropipetted and added onto the hydrophobized carrier (5 µL). Then, the carrier was dried in a hot air oven for 30 min at 60 °C in order to evaporate the solvent and get a thin dried residue, which is analyzed by TXRF after cooling at open air for 1 h. All samples were measured in triplicate by its deposition on three different carriers.

Gain correction. Before each series of measurements, a carrier with arsenic (As) standard was run in the TXRF to compensate possible drifts of the spectroscopic amplification and accurately locate the fluorescence lines in the spectrum by means of the known fluorescence peak and signal of As.

Element analyses were performed with a portable benchtop Bruker TXRF spectrometer S2 Picofox, with molybdenum-anode excitation, a silicon drift detector and a generator of 50 keV maximum power. Unless otherwise stated, the samples were measured for 600 s and at 15 mA, under a standard method and configuration that ensure the best excitation and detection conditions in TXRF, at a current of 600 µA, stop condition at 100 s of life time, filter 9 µm, monochromator 17.5 keV, ambient air and energy range from 0 to 20 keV. Because of the complexity of the X-ray spectra, corrections were made for the escape peak, pile ups and an automatic background subtraction (maximum 1000 stripping cycles of 50 step width).

The spectra were analyzed using the conventional software Bruker Spectra Picofox 7.5.3.0 (Copyright Combit® GmbH 1991-2009) that automatically determines the intensities of the characteristic X-ray peaks for the elements and quantifies their concentration according to the sensitivity factors (Eq. 1). The sensitivity factors determine the fixed calibration functions for each element and therefore it is possible to perform an internal standardization. The calibration, normalization and blank correction used in this work are described in the Supplementary Information (SI).

$$C_i = \frac{C_{IS} \cdot N_i \cdot S_{IS}}{N_{IS} \cdot S_i} \quad (1)$$

where C_i is the measured concentration of the analyte i, C_{IS} is the concentration of the internal standard (IS), N_i is the net pulse number of the analyte i (counts) in the measured spectrum, S_{IS} is the relative sensitivity of the IS element, N_{IS} is the net pulse number of the IS (counts) in the measured spectrum and S_i is the relative sensitivity of the analyte i.[5]

In addition to the elements present in the dried residue, silicon from the quartz glass carrier, argon from the air gap between the detector and the carrier and molybdenum from the scattered primary beam, gave intensive signals of Kα lines at 1.7, 3.0 and 17.5 keV, respectively, in all spectra.

To assess the accuracy and concordance between the measured concentrations (C_{Ni}) and the calculated theoretical ones (C_T), recovery rates (RR in %) were used, as they frequently appear in analytical studies (Eq. 2).

$$RR\ (\%) = \frac{C_{Ni}}{C_T} \times 100 \quad (2)$$

To assess the precision, reproducibility and random error of the measurements, the relative standard deviation (RSD in %) was used for the ease of comparing (Eq. 3).

$$RSD\ (\%) = \left(\frac{\sqrt{\frac{\sum_{i=1}^{N} (C_{Ni} - \overline{C_{Ni}})^2}{N-1}}}{\overline{C_{Ni}}} \right) \times 100 \quad (3)$$

where $\overline{C_{Ni}}$ is the average normalized concentration of the analyte i and N is the number of measurements.

For graphical representations, the standard deviation (SD in concentration units or in number of counts) was depicted as vertical error bars in the figures (Eq. 4).

$$SD = \left(\sqrt{\frac{\sum_{i=1}^{N} (X_i - \overline{X_i})^2}{N-1}} \right) \quad (4)$$

where X_i is the measured concentration or counts of the analyte i, $\overline{X_i}$ is the average concentrations or counts of the analyte i, N is the number of measurements.

RESULTS AND DISCUSSION

Efforts were made to specifically select the metals of analysis that would secure a wide representability of the most challenging and common samples to be measured in research. In that sense, the first group of selected elements were those that have their K or L lines lying near the K lines of the most common matrix components: potassium (K) and calcium (Ca). The selected elements were transition metals (manganese, Mn; chromium, Cr; cobalt, Co), traditional metals in technical applications and in pollution studies[38,39] (higher intense K lines), and the lanthanides (lanthanum, La; cerium, Ce; praseodymium, Pr; neodymium, Nd; samarium, Sm;

europium, Eu; gadolinium, Gd; terbium, Tb; dysprosium, Dy; holmium, Ho; erbium, Er; thulium, Tm; ytterbium, Yb and lutetium, Lu), critical metals in terms of high economic value and supply risk[40] used in magnets, lamp phosphors and NiMH batteries (low-intensity L lines). The second group of selected elements were those that are detected using their high-intensity K lines, *i.e.*; yttrium (Y) and strontium (Sr), because in this case these fluorescence lines are lying near the strong K line peak of molybdenum (the X-ray source), potentially leading to problems in the deconvolution of the peaks. Finally, gallium (Ga) was included because it is frequently used as internal standard since it is usually absent from the samples.

The salt $CaCl_2$ was used to vary the concentration of the inorganic matrix, as calcium-rich matrices show a substantial matrix effect, decreasing drastically the signal of the analytes.[41] In addition, chloride is the most common anion of salt matrices in aqueous samples and, although calcium is not as common as sodium, its atomic mass is almost double than that of sodium, resulting in a heavier matrix element. A matrix containing heavy elements causes an under- or overestimation of the analyte concentration more pronounced than a matrix with lighter elements. Thus, calcium ensures a worst-case scenario in comparison to sodium. Trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) was used to vary the concentration of the organic matrix, relevant to analyses of organic-like samples, which are difficult to measure with other techniques. This long-chain phosphonium $C_{32}H_{68}ClP$ is water-immiscible and has a higher viscosity (1800 cP, 25 °C) and lower density (0.8819 g cm^{-3} at 25 °C) than water. Finally, Triton™ X-100 was employed because it is generally used,[3,39] together with other organic stabilizing agents and surfactants,[31,42] to improve the homogeneity of sludges,[43] slurries,[31] and solids samples, prior to TXRF analysis.

The absorption of secondary fluorescence X-rays by inorganic media was studied by varying the concentration of $CaCl_2$ in solutions containing 50 mg L^{-1} of each Nd, Ga and Pr (Figure 1). Nd simulated the analyte and both Ga and Pr played the role of internal standard. These elements were selected because Ga is often used as internal standard and Pr has a similar energy of the measured X-ray fluorescence line to the analyte Nd, which could significantly improve measurements under the influence of a matrix absorbing secondary fluorescence X-rays,[30,36] and it is here referred to as *optimum internal standard* (OIS). In the absence of $CaCl_2$, the measurements of Nd corresponded to the expectations (100% RR), regardless of whether IS or OIS was used. However, when increasing the concentration of $CaCl_2$, the RRs of Nd became poor, being significantly lower than the expected 100% when using Ga as internal standard. Thus, when 5.55 g L^{-1} $CaCl_2$ was present, Nd was underestimated more than 70% of the true value with Ga as IS, whereas in a 10 fold more concentrated $CaCl_2$ solution (55.49 g L^{-1}), Nd was underestimated by only 5% with Pr as OIS. When the concentration of $CaCl_2$ was 140 g L^{-1}, the large deviation resulted in poor results (vertical error bars in Figure 1), even when using an OIS. This is explained by the difference in morphology between the three sample depositions (triplicate) arising from the large amount of $CaCl_2$ present.

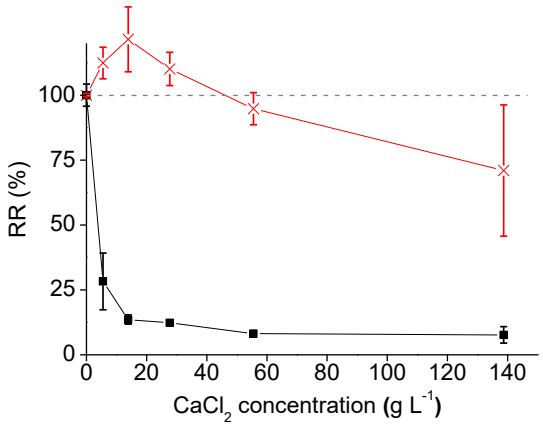


Figure 1. Recovery rates (RR) of 50 mg L^{-1} Nd (triplicate measurements) diluted in ultrapure water as a function of the $CaCl_2$ concentration with 50 mg L^{-1} of ■ Ga (IS) and X Pr (OIS) after internal standardization. Dash line: point without $CaCl_2$ matrix.

When, instead of ultrapure water, an aqueous solution of Triton™ X-100 (53.5 g L^{-1}) was used for dilution during the internal standardization, the results significantly improved, with RRs between 104 and 110% when using the OIS (Figure 2). The RRs of Nd were slightly higher than the expected 100% due to the lower energy of the fluorescence X-rays of the OIS (in comparison to Nd) which are therefore more likely to be absorbed by the matrix. In addition, a stable RR was observed as a function of increasing the $CaCl_2$ concentration (Figure 2), with significantly lower RSDs than previously observed without Triton™ X-100 (Figure 1). The poorer recoveries when using Ga as IS than when using OIS corroborate the improvement when using an OIS in solutions with high salt concentrations.

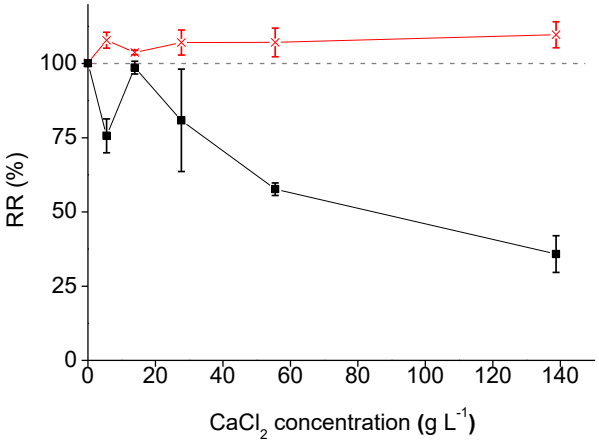


Figure 2. Recovery rates (RR) of 50 mg L^{-1} Nd (triplicate measurements) diluted in Triton™ X-100 (53.5 g L^{-1} in water) as a function of the $CaCl_2$ concentration with 50 mg L^{-1} of ■ Ga (IS) and X Pr (OIS) after internal standardization. Dash line: point without $CaCl_2$ matrix.

When comparing the number of counts between the measurement of the samples diluted in water and Triton™ X-100, the influence of the $CaCl_2$ content and the importance of Triton™ X-100 dilution becomes even more pronounced. If the number of counts is taken into account, an increasingly reduction of the counts occurred as the $CaCl_2$ content increased (Figure 3). The decrease in counts resulting in a lower excitation radiation intensity is due to the reduction of X-ray standing wave field intensity. The absorption of primary and secondary X rays by the matrix, reduces the probability to excite the element of interest (and IS) and to detect the emitted photons. Yet the decrease in the total number of counts of Nd (and IS) was much less significant when using 53.5 g L^{-1} Triton™ X-100 as diluent in the internal standardization, than when using only water (Figure 3). For instance, with Triton™ X-100, the counts of Nd decreased by a factor of 3 in a 55.49 g L^{-1} $CaCl_2$ matrix, whereas without this surfactant they decreased by a factor 150. This graphically resulted in more intense peaks in the TXRF spectra (Figure S1).

Furthermore, increasing the $CaCl_2$ content resulted in poor data reproducibility, as revealed by the high SDs of the number of counts of Nd in the presence of $CaCl_2$ compared to the SD of the number of counts in the absence of $CaCl_2$ (vertical error bars in Figure 3, logarithmic scale). Yet, the loss in reproducibility was much less significant when diluting with Triton™ X-100 (RSDs of counts from 5 to 30%, when $CaCl_2$ from 0 to 140 g L^{-1}) than when diluting with ultrapure water (RSDs from 5 to 123%). For instance, by using Triton™ X-100 in the internal standardization, the RSD of the number of counts of Nd increased by a factor of 6 in a 140 g L^{-1} $CaCl_2$ matrix, whereas the number of counts when using pure ultrapure water increased by a factor of 25 at the same $CaCl_2$ concentration. The high variation in the number of counts at high $CaCl_2$ concentrations shows that TXRF analysis by external calibration of high-salt containing solutions can lead to large errors, even when preparing the calibration standard solutions with the same salt content as the samples. This is because the high RSDs cause large uncertainty intervals in the concentrations calculated by the correction factors (Eq. 1) of theoretical and external calibrations curves, reducing the precision of the measurements. The preferred option for measuring samples containing high-salt matrices is therefore the internal standardization method which provides a proportional reduction of the counts absorbed by the matrix for both analyte and OIS (Figure 3).

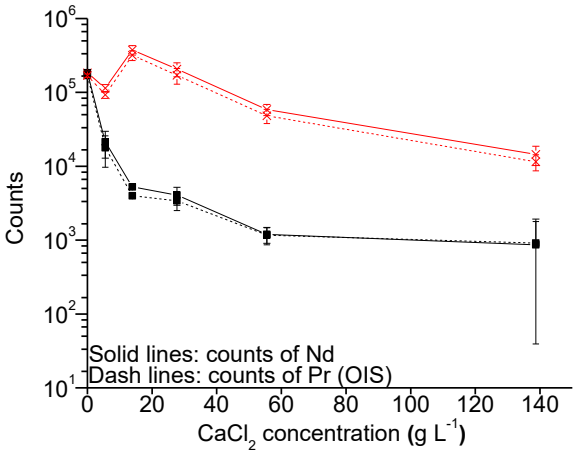


Figure 3. Logarithmic Y-axis: Number of counts of 50 mg L^{-1} Nd and 50 mg L^{-1} Pr (triplicate measurements) diluted in 53.5 g L^{-1} of Triton™ X-100 (X) or ultrapure water (■) as a function of the $CaCl_2$ concentration with 50 mg L^{-1} Pr (OIS) after internal standardization.

The amount of Triton™ X-100 plays an important role in the obtained RSD values. For instance, for a salt concentration of 140 g L^{-1} $CaCl_2$, a concentration of Triton™ X-100 of ≥ 32 g L^{-1} after internal standardization assured the lowest RSD (1%) which is comparable to RSD values found in low-salt solutions (0.7-1.4%).[36] A higher concentration of Triton™ X-100 (53.5 g L^{-1}) did not result in any improvement of results, while concentrations lower than 10 g L^{-1} of Triton™ X-100 after internal standardization resulted in higher RSD (>10%).

It was visually observed that the presence or absence of Triton™ X-100 led to different morphologies of the dried residue (sample deposited on the carrier after evaporating the solvent). In the absence of Triton™ X-100, the dried residue formed on the sample carrier was cone-like shaped, suggesting particle aggregation and local accumulation of elements in the centre of the sample cone, which undermines the much-needed principle of thin-sample preparation for TXRF. Similarly, the widely recognized "coffee-ring" formation causes absorption of secondary X-rays due to an inhomogeneous distribution of material in the outer border of the circle.[30] Conversely, when using Triton™ X-100, the deposited sample was uniformly distributed over a larger surface on the carrier and the layer was thinner, so that reproducible drops could be obtained on the sample carriers (Figure S2). This might be related to the better results obtained with Triton™ X-100.

As aqueous samples differ widely between them according to their composition, the next step was to compare two different aqueous matrices: NH_4NO_3 and $CaCl_2$. Depending on the nature of the X-ray absorbing or scattering elements, more or less X-rays will be absorbed or scattered, affecting the accuracy of the results. In the absence of Triton™ X-100, the RRs of Nd in samples with a high NH_4NO_3 content were better than with a high $CaCl_2$ content (Figure 4). This may be due to the heavier atoms in $CaCl_2$ compared to NH_4NO_3. In any case, the results in both media improved considerably if Triton™ X-100 was used during the internal

standardization (Figure 4). In order to avoid wrong results, it is advised to dilute samples containing heavy elements salts with a Triton™ X-100 solution as much as the detection limits allow.

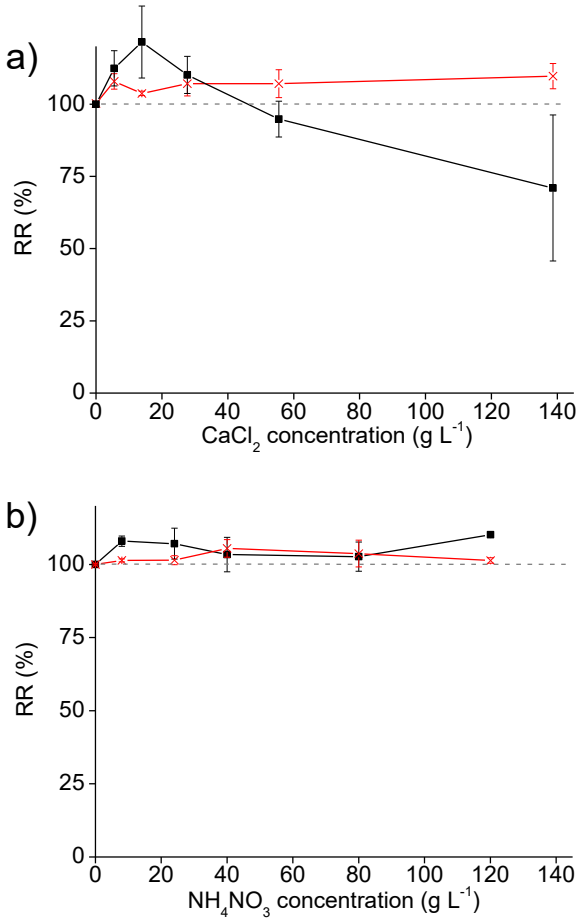


Figure 4. Comparison of the recovery rates (RR) of 50 mg L^{-1} Nd (triplicate measurements) diluted in Triton™ X-100 (X) or ultrapure water (■) with 50 mg L^{-1} of Pr (OIS) between two salt matrices: (a) $CaCl_2$ and (b) NH_4NO_3. Dash line: point without $CaCl_2$ or NH_4NO_3 matrix.

Commonly, aqueous samples consist of more than one element of interest having all different concentrations. Therefore, samples with 20 elemental standard solutions in a $CaCl_2$ medium were studied. The composition of the samples consisted of Mn, Cr, Co, Ga and Sr (50 mg L^{-1} each one) and the lanthanides plus Y (10 mg L^{-1} each one, except for Eu which was 3 mg L^{-1}), with $CaCl_2$ concentrations ranging between 0 and 140 g L^{-1}. If no $CaCl_2$ was present, good RRs for all different elements were achieved no matter which IS was chosen, with an average RSD of 10.7% (Table S1). However, when $CaCl_2$ was present and without Triton™ X-100, the RSD of the RRs for all different elements increased from 11% (no $CaCl_2$) to 50, 192, 255 and 600% as a function of the increasing $CaCl_2$ content to 6, 56, 97 and 140 g L^{-1}, respectively (Table S2, Table S3, Table S4 and Table S5). In the presence of $CaCl_2$ and no Triton™ X-100, the best RRs were obtained with an OIS having a concentration close to the one of the analyte. This is consistent with previous research that studied the influence of the concentration of the IS in determining the levels of a multi-elemental solution.[37] Also the calibration affects the results, as the best RRs are obtained when measuring analyte and IS at the same concentration ratio at which both elements are calibrated relative to each other.[36]

It was also observed that above a threshold matrix content or below a certain analyte concentration, it is not possible to determine the concentration of the elements (analytes and standards) with peaks/energies very similar to the matrix elements. This is because the peak of the matrix element is too wide and overlaps with the analyte and/or standard peak(s), increasing the limit of detection (LOD). La, Ce, Pr and Nd have the closest X-ray fluorescence lines to the one of the matrix element Ca. When measuring in a matrix of 5.55 g L^{-1} $CaCl_2$ and no Triton™ X-100, the RRs of La and Ce dropped to 74 and 78% using the OIS (Table S2). When the matrix was equal to or higher than 55.5 g L^{-1} of $CaCl_2$ (Table S3, Table S4, Table S5), La, Ce, Pr and Nd were no longer detectable (0% RRs). Therefore, in the absence of surfactant, precautions should be taken when measuring low concentrations of elements with X-ray intensities near to the intensities of the matrix elements, on a case-by-case basis.

The effect on the TXRF measurements of such high salt concentration cannot be predicted since it is not possible to obtain a thin and homogenous dry residue on the carrier. However, the use of the surfactant Triton™ X-100 can maintain low LOD of trace element analysis by TXRF. To check this, a sample that consisted of the above 20 elements with a 27.75 g L^{-1} of $CaCl_2$ matrix after internal standardization (0.980 mole fraction of the matrix compound) was selected for comparing the results obtained with and without Triton™ X-100. This sample could serve as example for trace analysis of low analyte concentrations present in high-salt solutions. The results revealed that the recovery and the reproducibility of the data are better when using the surfactant (Figure 5, Table 1). Using Triton™ X-100 allows the measurement of elements with lower-intensity L-lines which are conventionally difficult to analyze by a TXRF spectrometer with a molybdenum Kα source, in a matrix of elements that generate strong spectrum lines, such as calcium-containing matrices.[39] In previous studies by Stosnach, inaccurate results for Cr, Ni and As (39, 27, 27 mg L^{-1}, respectively) were obtained without surfactant in a matrix of Na, Mg and Ca (0.725, 0.136, 0.100 mole fraction, respectively).[39] In the present work, Cr (50 mg L^{-1}) is successfully recovered at a RR of 98.8 ± 0.4% in a sample with Triton™ X-100 and a 0.980 mole fraction of Ca (Figure 5, Table 1). Additionally, in Stosnach's study, spectral interferences were observed between the peaks of Pb and As, and between Cu and Ni, when the concentrations of Pb and Cu are 10 times higher than those of As and Ni.[44] In the present work, the analytes located close to each other, even with a difference in their concentration of 5 and 17 times (e.g., Cr and Sm, and Cr and Eu, respectively) did not show significant spectral interferences.

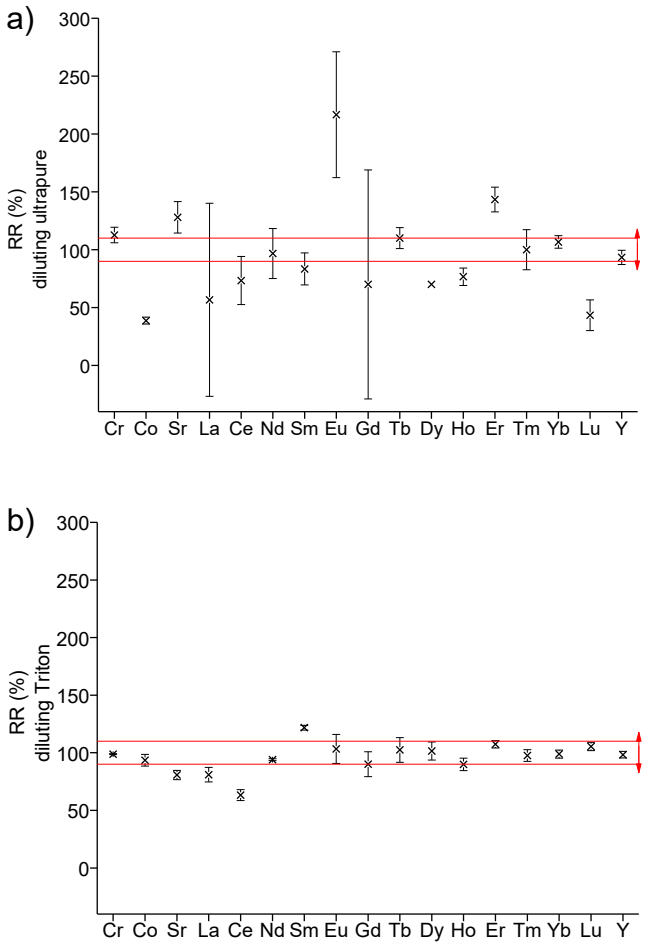


Figure 5. Recovery rates (RR) of 20 elements (0.005 M) in a matrix of 27.75 g L^{-1} of $CaCl_2$ (0.980 mole fraction) diluted in (a) ultrapure water or (b) a solution of 53.5 g L^{-1} Triton™ X-100, using the OISs of Table 1 (triplicate measurements). The red box outlines the area within 10% of deviation from the 100% RR.

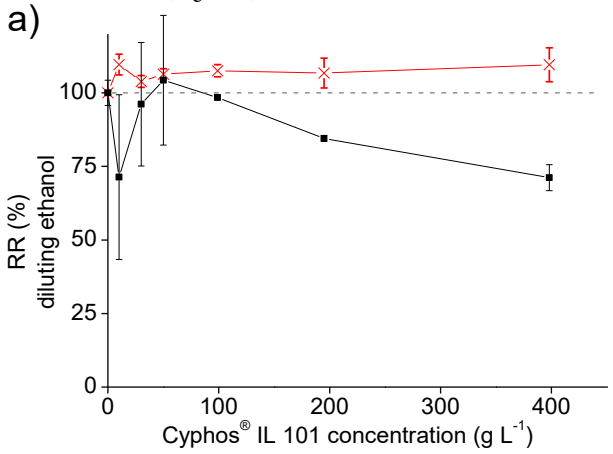
Table 1. Concentrations (C, in mg L^{-1}), optimum internal standard (OIS) chosen to quantify the analytes (RR reported in Figure 5) and concentration ratios of the OIS to the analyte ($C_{OIS}/C_{Analyte}$).

Analytes	$C_{Analyte}$	OIS	C_{OIS}	$C_{OIS}/C_{Analyte}$
Cr	50	Mn	50	1
Co	50	Ga	50	1
Sr	50	Ga	50	1
La	10	Pr	10	1
Ce	10	Pr	10	1
Nd	10	Pr	10	1
Sm	10	Mn	50	5
Eu	3	Mn	50	17
Gd	10	Mn	50	5
Tb	10	Mn	50	5
Dy	10	Co	50	5
Ho	10	Co	50	5
Er	10	Co	50	5
Tm	10	Co	50	5
Yb	10	Co	50	5
Lu	10	Sr	50	5
Y	10	Sr	50	5

An increase in the number of counts for Nd was also observed for the 20-element mixture when using Triton™ X-100 instead of using ultrapure water. This can be visualized when displaying the spectra and comparing the size of the peaks at an equal y-scale (Figure S1). This shows the feasibility of using a solution of Triton™ X-100 for multi-element analysis of analytes in different concentrations.

Considering that TXRF can also measure organic samples such as oil-like substances, the RRs of 50 mg L^{-1} of Nd in viscous and organic samples were studied using Cyphos® IL 101 to vary the concentration of the organic matrix. As Cyphos® IL 101 is water immiscible, the internal standardization was performed by diluting with ethanol.

The RRs of Nd were close to 100% and had very low RSD values when using the OIS and ethanol over a larger range of Cyphos® IL 101 concentrations than when using a solution of 107 g L^{-1} Triton™ X-100 in ethanol (Figure 6).



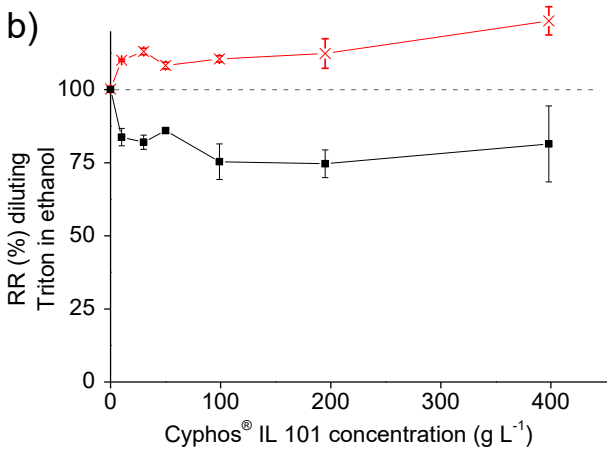


Figure 6. Recovery rates (RR) of 50 mg L^{-1} Nd (triplicate measurements) diluted in (a) ethanol or (b) a solution of 107 g L^{-1} Triton™ X-100 in ethanol as a function of the Cyphos® IL 101 content with 50 mg L^{-1} of ■ Ga (IS) and X Pr (OIS), after internal standardization. Dash line: point without Cyphos® IL 101 matrix.

Measurements of Cyphos® IL 101 with dilutions in ethanol usually resulted in more counts than a dilution in a mixture of Triton™ X-100 and ethanol (Figure 7). Ethanol extends the deposited sample drop in the carrier over a larger surface, preventing an inhomogeneous accumulation of mass, in favour of a good spreading and an *infinitely thin sample*. This indicates that probably also other alcohols and surfactants can be used as stabilizing agents for TXRF analysis.[31] Here, Triton™ X-100 and ethanol were tested, but polyvinyl alcohol (a water-soluble synthetic polymer applied in coatings with an idealized formula $(C_2H_4O)_n$) can also be used to achieve a thin and homogenous dried residue on the carrier.[42,45]

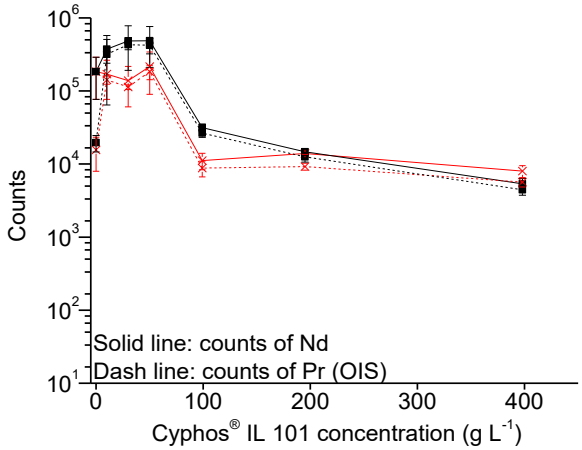


Figure 7. Logarithmic Y-axis: Number of counts of 50 mg L^{-1} Nd and 50 mg L^{-1} Pr (triplicate measurements) diluted in 107 g L^{-1} Triton™ X-100 in ethanol (X) or ethanol (■) as a function of the Cyphos® IL 101 content with 50 mg L^{-1} Pr (OIS), after internal standardization.

To check whether the use of a surfactant remains satisfactory to directly analyze low concentrations of analytes in high-salt solutions, the tests on $CaCl_2$ (0–140 g L^{-1}) and on Cyphos® IL 101 (0–194.78 g L^{-1}) were repeated but for a Nd concentration of 5 mg L^{-1}. These concentrations are relevant for aqueous samples from waste water and pollution studies, where the analyte in the samples solutions can be present in relatively low concentrations. The results showed a higher impact on the spectral resolution and on the RRs when increasing the $CaCl_2$ content than when increasing the Cyphos® IL 101 concentration (Figure 8). The worst RRs in case of $CaCl_2$ were due to the increase in the molar ratio between the matrix element and the analyte, which led to a much lower number of counts compared to Cyphos® IL 101 and higher LOD (Figure 8.b). Nevertheless, a previous work with samples that had an even much lower matrix content (7–10 g L^{-1} of active pharmaceutical ingredients) and thus a lower absorption of secondary X-rays, observed poor RRs when the analyte concentrations decreased from 5 to 0.1 mg L^{-1}, applying the conventional TXRF analysis procedure.[27] In that study, using 3.3–5 mg L^{-1} of Ga as IS, the RRs of Ca, K, Fe and Pd remained around 100% for concentrations between 5 and 50 mg L^{-1}, but at 0.1 mg L^{-1}, the RRs of those elements worsened to 50, 150, 200 and 300%, respectively.[27]

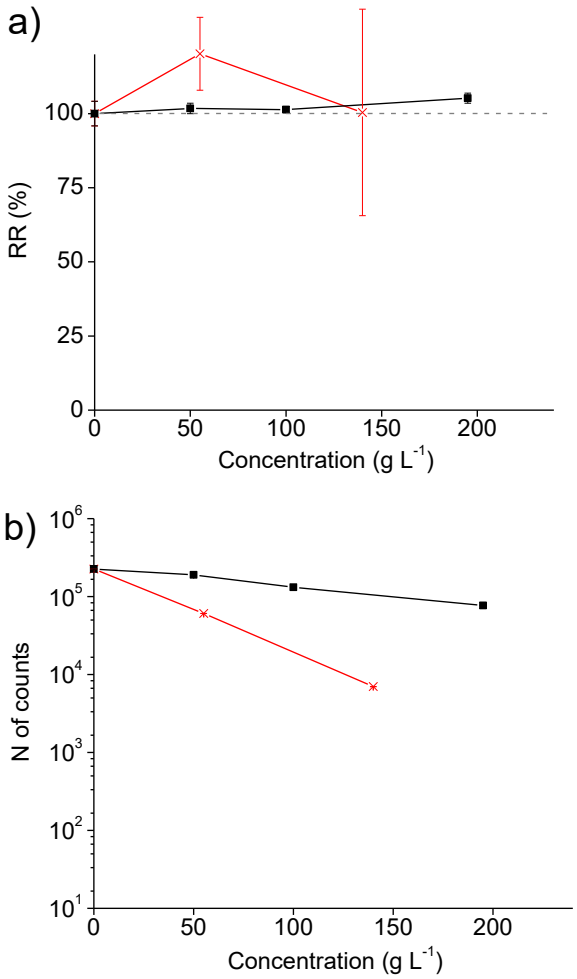


Figure 8. Recovery rates (RR) (a) and number of counts (logarithmic Y-axis) (b) of 5 mg L^{-1} Nd (triplicate measurements) with 5 mg L^{-1} Pr (OIS) after internal standardization. (X): diluted in a solution of Triton™ X-100 as a function of the $CaCl_2$ content. (■): diluted in ethanol as a function of the Cyphos® IL 101 content.

For the $CaCl_2$ matrix, it is not possible to quantify the concentrations with satisfactory reproducibility and accuracy when Nd is below the concentration of 5 mg L^{-1}. In this case, care must be taken to avoid carrier surface contamination during both the TXRF sample preparation and the carriers cleaning process. Carrier contamination prevents accurate analyses, which are further exacerbated in the case of low concentrations of analytes and because of the low LOD of TXRF.

CONCLUSIONS

Matrix effects constitute the major sources of errors in X-ray fluorescence analysis due to the absorption of secondary X-rays by the matrix elements and the difference in the energy of the fluorescence X-rays of the analyte compared to the one of the matrix element and the one of the internal standard. Matrix effects can lead to either under or overestimation of the true concentration of an analyte, depending on whether the analyte and the matrix element are located at a node and antinode respectively of the standing waves (underestimation) or at an antinode and node respectively (overestimation). The effect of the absorbed and enhanced X-rays on metal quantification in the TXRF (matrix effect), was studied for aqueous and organic solutions. The liquid samples (3–20 elements) were measured at different $CaCl_2$ (0–140 g L^{-1}), NH_4NO_3 (0–120 g L^{-1}) and Cyphos® IL 101 (0–397.6 g L^{-1}) concentrations (after internal standardization) using different ISs and diluents (water, ethanol and their mixtures with Triton™ X-100). Improved RRs and RSDs were achieved for analyte concentrations of 50 mg L^{-1} when diluting the samples with an aqueous solution of Triton™ X-100 in case of a $CaCl_2$ matrix or with pure ethanol in case of a Cyphos® IL 101 matrix. This also applies to elements with X-ray energies near to the energies of the matrix elements, which would not be possible to detect without the use of the surfactant. Inorganic samples containing light elements have a minor negative impact on the recoveries than samples with heavy elements. In the last case, samples should be diluted with a Triton™ X-100 solution as much as the LOD allows and the dilution error remains insignificant. At low metal concentrations (5 mg L^{-1}), the RRs and RSDs with large Cyphos® IL 101 matrices were much better than the ones with large $CaCl_2$ matrices, due to the increase in the molar ratio Ca/analyte. Using the OIS in a concentration comparable to that of the analyte and diluting with an aqueous solution of Triton™ X-100 (for inorganic salts) and pure ethanol (for organic salts) is proposed here for routine elemental determination by TXRF in samples with matrices. Thanks to internal standardization, the higher counting variation in case of external calibration is avoided. Diluting the samples with Triton™ X-100 or ethanol leads to uniform, well spread, thin and reproducible dried sample residues onto the hydrophobized sample carriers, which prevents local inhomogeneous aggregation of elements and increases the counts and measurement precision. The spectra reviewed had high signal-to-noise ratios and reasonable count rates. This procedure requires no special equipment, no mathematical corrections experimentally derived from reference samples and no interfering-elements removal by pH adjustment-precipitation-filtration-washing-drying, or by chelation-selective adsorption-elution, allowing more analyses per unit of time.

SUPPORTING INFORMATION

The Supporting Information (SI) is available free of charge on the ACS Publications website at DOI: …
The SI includes the calculation of the sensitivity factors, figures and tables.

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Author Contributions

The manuscript was written through contributions of all authors.

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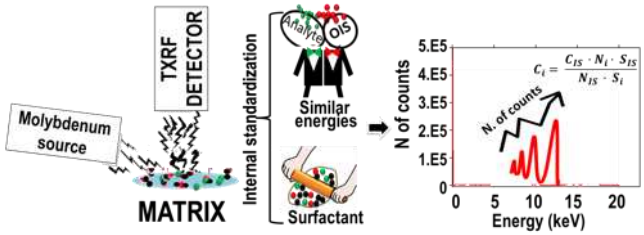
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Molybdenum source
MATRIX
Internal standardization
Analyte
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Similar energies
Surfactant
N of counts
Energy (keV)
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