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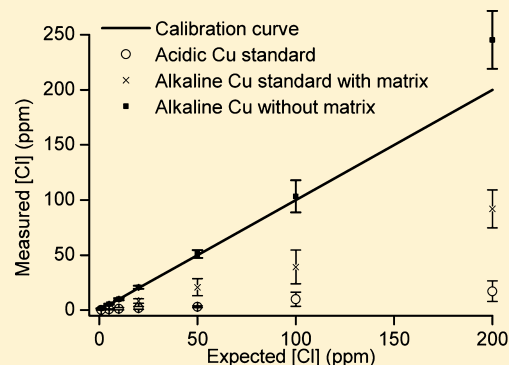
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# Determination of Halide Ions in Solution by Total Reflection X-ray Fluorescence (TXRF) Spectrometry

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**ABSTRACT:** An accurate quantitative determination of halide ions X (X = Cl, Br, I) in aqueous solution by total reflection X-ray fluorescence (TXRF) is not possible using the traditional acidic internal standards. In general, the standard solutions are highly acidic (e.g.,  $\text{Ga}(\text{NO}_3)_3$  in  $\text{HNO}_3$ ) to avoid precipitation of hydroxides of the standard element and to obtain a stable and reliable standard. In acidic solutions, dissolved halide salts can exchange their cation for a proton. The resulting volatile HX compounds can evaporate during the drying procedure of the TXRF sample preparation. In this technical note, we show that an alkaline  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$  standard can be used for the determination of chlorine, bromine and iodine without facing problems of HX evaporation.



Total Reflection X-ray Fluorescence (TXRF) spectroscopy is an analytical technique for simultaneous multielement analysis in liquids, solids and suspensions.<sup>1–9</sup> It can detect almost all elements of the periodic table, except the lightest ones, which are less sensitive to primary X-rays. The detection limits are into the low ppb range or even ppt range for X-ray sensitive elements such as bromine.<sup>10</sup> The main difference with conventional techniques such as energy-dispersive X-ray fluorescence (EDX) is that the sample is irradiated with monochromatic X-rays under a very small incident angle, so that the beam is therefore totally reflected.<sup>11,12</sup> Absorption and scattering of X-rays by the sample or matrix are significantly reduced compared to conventional XRF. Quantification of elements in solution can be done very easily by addition of an internal standard, i.e., an element which is not present in the sample. In principle, a calibration curve for a specific matrix has to be made only once. The simplicity of the technique and the short analysis time are major advantages of TXRF. After adding the internal standard to the sample (typically an acidic gallium solution is used), a small amount of the solution is pipetted onto a sample carrier (e.g., quartz glass) and further dried to obtain only solid particles on the carrier. Depending on the concentration and the elements present in the sample, the composition can be determined very fast after measuring the sample spectrum. Other advantages of the TXRF technique include small sample amounts, low maintenance cost, limited consumption of chemicals and the possibility to measure a broad variety of samples ranging from solutions to solids, viscous oils or organic solvents.<sup>13–28</sup>

The determination of halide ions in solution is important for different applications. Many analytical techniques have been developed already for the determination of halides. Examples include ion chromatography,<sup>29–31</sup> capillary zone electrophoresis,<sup>32,33</sup> atomic emission spectroscopy,<sup>34,35</sup> mass spectroscopy,<sup>36,37</sup> spectrophotometric methods with fluorescent in-

dicators,<sup>38,39</sup> argentometry,<sup>40</sup> or electrochemical techniques.<sup>41–45</sup> Most of these techniques ask for the construction of a calibration curve, they are time-consuming and require the use of large amounts of solvents or reagents. These technical issues are not applicable to TXRF measurements. On the other hand, the determination of halide ions with TXRF is challenging. The internal standard, added to the samples, is often acidified to obtain a stable metal standard that is not susceptible to hydrolytic reactions. However, halide salts can react with the acid present in the mixture and form volatile HX compounds, which are lost during the drying step of the sample preparation procedure.<sup>46–50</sup> Several attempts to avoid losses of halides have been made in the past. Halide ions can be measured indirectly by precipitating the halide ions with  $\text{AgNO}_3$  and measuring the excess of silver,<sup>47</sup> or by adding  $\text{AgNO}_3$  to the sample on the carrier.<sup>46</sup> Dhara et al. used a cobalt standard in alkaline conditions to measure chlorine.<sup>48</sup> No hydrolysis or precipitation of the cobalt standard was reported even though they worked in alkaline conditions. Tarsoly et al. used a neutral  $\text{NH}_4\text{VO}_3$  standard for the determination of fluorine.<sup>49</sup>

Alkaline or at least neutral conditions are required to measure halides with TXRF and to avoid halide losses. In this technical note, we evaluated metal salts soluble in alkaline aqueous solutions and selected the tetraamminecopper(II) nitrate complex  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$  for the determination of chlorine, bromine and iodine present as potassium salts in solution. The alkaline copper standard was compared with a traditional acidic copper standard.

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## ■ EXPERIMENTAL SECTION

**Chemicals.** Standards of copper(II) nitrate ( $1000 \text{ mg L}^{-1} \text{ Cu}$ ), potassium bromide ( $1000 \text{ mg L}^{-1} \text{ Br}$ ), potassium iodide ( $1000 \text{ mg L}^{-1} \text{ I}$ ) and gallium(III) nitrate ( $1000 \text{ mg L}^{-1} \text{ Ga}$ ) were purchased from Chem-Lab NV (Zedelgem, Belgium). The potassium chloride standard ( $1000 \text{ mg L}^{-1} \text{ Cl}$ ) was purchased from Mettler–Toledo (Zaventem, Belgium) and copper(II) nitrate dihydrate (99.999%) from Sigma-Aldrich (Diegem, Belgium). The silicone solution in isopropanol was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany). The ammonia solution (25 wt %) and nitric acid (65 wt %) were purchased from Chem-Lab NV (Zedelgem, Belgium). The detergent RBS 50 pF was obtained from Chemical Products R. Borghgraef (Brussels, Belgium). Dilutions were made with  $18.2 \text{ M}\Omega\cdot\text{cm}$  Milli-Q water.

**Calibration Solutions.** Two-hundred microliters of the acidic copper standard was mixed with  $600 \mu\text{L}$  of a 2.5 wt %  $\text{NH}_3$  solution for the calibration points constructed with the alkaline standard. Two-hundred microliters of the potassium salt standard was added to obtain an alkaline solution ( $\text{pH} \approx 11$ ) containing  $200 \text{ mg L}^{-1}$  of the halide and  $200 \text{ mg L}^{-1}$  of copper. Five-hundred microliters of this solution was removed and diluted to 1 mL with a 2.5 wt %  $\text{NH}_3$  solution in which a solution containing  $100 \text{ mg L}^{-1}$  of halide and  $100 \text{ mg L}^{-1}$  of copper was obtained. This solution was again diluted in an identical way to obtain a solution containing  $50 \text{ mg L}^{-1}$  of both elements. Concentrations of 20, 10, 5 and  $1 \text{ mg L}^{-1}$  of copper and the halide were prepared using the same dilution procedure. The  $\text{NH}_4\text{NO}_3$ -free alkaline copper standard was prepared by dissolving  $0.192 \text{ g Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 65 mL of water. The concentration of this solution was measured by TXRF with an acidic gallium internal standard. The  $200 \text{ mg L}^{-1}$  solution was prepared by mixing  $200 \mu\text{L}$  of the  $1000 \text{ mg L}^{-1}$  KCl standard with the appropriate volume of the  $\text{Cu}(\text{NO}_3)_2$  solution. The mixture was then further diluted with a 2.5 wt %  $\text{NH}_3$  solution to a final volume of 1 mL to obtain  $200 \text{ mg L}^{-1}$  of copper and chlorine. The calibration solutions in acidic media were obtained by mixing  $200 \mu\text{L}$  of a  $1000 \text{ mg L}^{-1}$  acidic copper solution with  $200 \mu\text{L}$  of a  $1000 \text{ mg L}^{-1}$  halide salt solution. Dilution of this sample to 100, 50, 20, 10, 5, and  $1 \text{ mg L}^{-1}$  copper and halide was performed in the same way as described above for the alkaline samples. It was observed that measurements of halide concentrations lower than about  $1 \text{ mg L}^{-1}$  were inaccurate and imprecise. Matrix effects could occur when measuring high concentrations and such solutions should be diluted. Therefore, it was decided make calibration curves for concentrations between 1 and  $200 \text{ mg L}^{-1}$ .

**Equipment.** A Synergy UV water purification system has been used to obtain  $18.2 \text{ M}\Omega\cdot\text{cm}$  Milli-Q water. A benchtop Picofox S2 (Bruker Nano) total reflection X-ray fluorescence spectrometer with a molybdenum X-ray source has been used for all measurements. The voltage of the X-ray tube was 50 kV and the current  $600 \mu\text{A}$ . The spectra were corrected for escape and pile-up peaks, and the background was corrected by applying maximum 1000 stripping cycles with a step width of 50 in the profile bayes optimized fit mode. Sample carriers and glassware were cleaned in advance to avoid halide impurities by washing for 15 min with hot RBS 50 pF and with 10 wt % hot nitric acid for 2 h. After this cleaning procedure, the carriers and glasswork were rinsed with Milli-Q water and acetone and dried in an oven at  $90^\circ\text{C}$ . Sample carriers were checked on the TXRF instrument for remaining halide contaminations left after

the cleaning procedure with an absolute method. All carriers were first pretreated with  $5 \mu\text{L}$  of Serva silicone in isopropanol solution and dried for 5 min. Five microliters of each solution was added onto a clean carrier and dried in a hot air oven at  $60^\circ\text{C}$  for 15 min. Each series was measured six times with an acidic or alkaline copper standard and measured at different day times to incorporate errors made by drying. This was important for the acidic standard in which the results strongly depended on the heating time and temperature. Samples with chlorine and iodine were measured for 200 s if the concentrations were above  $20 \text{ mg L}^{-1}$ . Samples with lower concentrations were measured for 500 s to obtain higher peak intensities, well above the background noise. Samples with bromine were measured for 100 s as this is an X-ray sensitive element in which a significant number of counts can be obtained in a shorter time. Longer measuring times did not influence the recovery rates and relative standard deviations as the peak intensities were all well above the background. The sensitivity factors of the halides supplied by the TXRF manufacturer were used for the initial calibration. It should be noted that TXRF is an element-specific method, so that the elements chlorine, bromine, iodine are measured rather than the ions chloride, bromide and iodide.

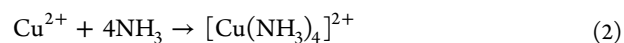
**Formulas and Calculations.** The recovery rates (RR) were calculated by dividing the average determined halide concentration values by the expected value. The relative standard deviations (RSDs) were calculated by dividing the standard deviation by the average determined value. The detection limits ( $C_X$ ) of the halides X were calculated by the PICOFOX software via eq 1:

$$C_X = \frac{C_{\text{Cu}} N_X S_{\text{Cu}}}{N_{\text{Cu}} S_X} \quad (1)$$

where  $N$  is the number of counts of the internal standard copper (Cu) or the halide (X),  $S$  is the relative sensitivity and  $C$  is the concentration of the elements.

## ■ RESULTS AND DISCUSSION

**Choice of Standard.** Alkaline or at least neutral conditions are necessary to avoid losses of halides by HX evaporation during TXRF sample preparation. Some metals can form water-soluble hydroxides (alkali metals) or slightly soluble hydroxides (some of the alkaline earth metals). Other metals, such as gallium, zinc, indium, bismuth and aluminum become only soluble at very high pH values because they are amphoteric metals and can bind an extra hydroxide anion to form a negatively charged and soluble hydroxo complex. It is known that the transition metals chromium, manganese, cobalt, nickel, copper and zinc form stable water-soluble complexes with ammonia in alkaline conditions. For instance, copper(II) can form the tetraamminecopper(II) complex:

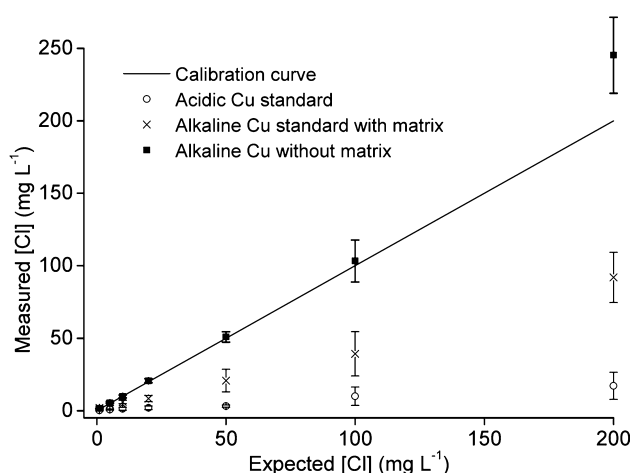


In our work, the tetraamminecopper(II) nitrate complex  $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$  was selected for several reasons: (1) the copper standard is one of the cheapest and best known standards. (2) It is a late 3d transition metal and less sensitive to matrix effects than the early 3d transition metals. (3) The excess of ammonia is evaporated during the drying process and does not leave a matrix behind whereas alkaline standards based on NaOH do. (4) The solubility of the standard is not dependent on the pH or the NaOH concentration. The

complex can be synthesized very easily by adding ammonia to a copper(II) salt such as copper(II) nitrate (eq 2, Figure 1).



**Figure 1.** Left: a matrix of  $\text{NH}_4\text{NO}_3$  on the sample carrier. Middle: acidic  $\text{Cu}(\text{NO}_3)_2$  standard. Right: the alkaline copper standard made by addition of  $\text{NH}_3$  to a  $\text{Cu}(\text{NO}_3)_2$  solution.



**Figure 2.** Plot of the recovered chloride concentrations with the acidic standard, the alkaline standard with  $\text{NH}_4\text{NO}_3$  matrix and the alkaline standard without  $\text{NH}_4\text{NO}_3$  matrix.

**Table 1. Recovery Rates (RR) and Relative Standard Deviations (RSD) of Chlorine with (1) an Acidic Standard, (2) an Alkaline Standard with  $\text{NH}_4\text{NO}_3$  and (3) Alkaline Standard without  $\text{NH}_4\text{NO}_3$  Matrix**

[Cl <sup>-</sup> ] (mg L <sup>-1</sup> )	acidic standard		alkaline standard with $\text{NH}_4\text{NO}_3$		alkaline standard without $\text{NH}_4\text{NO}_3$	
	RR (%)	RSD (%)	RR (%)	RSD (%)	RR (%)	RSD (%)
200	9	54	46	18	123	10
100	10	64	39	38	103	14
50	6	24	42	37	102	7
20	10	65	42	25	103	7
10	13	80	60	19	98	9
5	15	58	90	35	109	11
1	17	39	197	59	160	11

**Determination of Chlorides.** For the acidic samples, the recovery rates were between 6 and 17% and the relative standard deviations were high, ranging from 24 to 80% (Figure 2, Table 1). Also, the alkaline standard gave poor results in the first instance with recovery rates between 39 and 90% for concentrations between 5 and 200 mg L<sup>-1</sup> chlorine. The relative standard deviations were ranging from 19 to 39%. It was clearly observed that there was a significant amount of matrix on the sample carriers. This is due to the reaction between ammonia added to the acidic standard containing  $\text{HNO}_3$ , leading to the formation of  $\text{NH}_4\text{NO}_3$  (Figure 1).

Especially the lighter elements are very sensitive to matrix effects because their secondary low-energy X-rays are more strongly absorbed by the matrix than the X-rays produced by heavier elements.

A  $\text{Cu}(\text{NO}_3)_2$  standard without  $\text{NH}_4\text{NO}_3$  matrix was prepared by dissolving the salt in water and was calibrated by using a gallium internal standard. The recovery rates for this standard were close to 100%, except for 1 and 200 mg L<sup>-1</sup> chlorine. A concentration of 1 mg L<sup>-1</sup> is close to the detection limit, and small contaminations were inevitable so that a recovery rate of 160% was obtained. The RSD values were all below 15%. This value is better than the values obtained with the acidic standard or the alkaline standard with  $\text{NH}_4\text{NO}_3$  matrix.

**Determination of Bromides.** The secondary X-rays of bromine are higher in energy and less sensitive to matrix absorption than those of chlorine. Therefore, a matrix such as  $\text{NH}_4\text{NO}_3$  is not a problem for bromine. Recovery rates just below 100% were found for the highest concentrations. The recovery rates for samples with concentrations below 10 mg L<sup>-1</sup> were slightly higher but the RSD values were in all cases smaller than 10%. This is much lower than those of chlorine even without a matrix and it shows fact that secondary X-rays of bromine are less sensitive to matrix effects than those of chlorine (Table 2). All bromine samples were measured for only 100 s to prove that these measuring times were long enough to obtain precise and accurate results and to prove that the bromine concentrations could be measured very fast. A detection limit of 0.002 mg L<sup>-1</sup> was found for bromine.

**Table 2. Recovery Rates (RR) and Relative Standard Deviations (RSD) of Bromine with the Acidic and Alkaline Copper Standard**

[Br <sup>-</sup> ] (mg L <sup>-1</sup> )	acidic standard		alkaline standard	
	RR (%)	RSD (%)	RR (%)	RSD (%)
200	54	76	98	4
100	75	17	93	2
50	75	15	95	6
20	82	14	98	3
10	92	15	107	9
5	72	59	119	6
1	55	33	129	9

**Determination of Iodides.** The acidic and alkaline copper standards were tested for the determination of iodine as well. Evaporation of  $\text{HX}$  with the acidic standard was clearly observable in the case of chlorine, less pronounced for bromine and almost insignificant in the case of iodine. This is probably due to the lower volatility of  $\text{HI}$  (bp = -36 °C) in comparison to  $\text{HBr}$  (bp = -66 °C) and especially  $\text{HCl}$  (bp = -85 °C). The recovery rates for the acidic standard were between 49 and 98% but with high RSD values between 15 and 45%. Recovery rates between 79 and 93% were found for iodine when an alkaline standard was used (Table 3). The lower values could be due to absorption of the low energetic iodine X-rays by the  $\text{NH}_4\text{NO}_3$  matrix, as observed for chlorine. Iodine was measured on the low energetic L-line because the X-ray energies of the K-lines fall out of the spectrum when using a molybdenum X-ray source. On the other hand, a new sensitivity factor can be calculated with these results, which would be slightly lower than the one obtained from the TXRF manufacturer. The RSD values were lower than that in the case of the acidic standard and between 5 and 9% for concentration above values of 10 mg



**Table 3. Recovery Rates (RR) and Relative Standard Deviations (RSD) of Iodine with the Acidic and Alkaline Copper Standard**

[I <sup>-</sup> ] (mg L <sup>-1</sup> )	acidic standard		alkaline standard	
	RR (%)	RSD (%)	RR (%)	RSD (%)
200	86	36	83	5
100	98	30	89	8
50	94	15	84	6
20	87	16	79	7
10	66	38	93	9
5	49	43	85	22
1	75	45	76	53

L<sup>-1</sup>. At lower iodine concentrations, the recovery rates were higher, as were the RSD values. The same observation has been made for chlorine. This could be due to small contaminations or to the peaks with low intensity in combination with the overlapping potassium peak.

## CONCLUSIONS

In this technical note was shown that halide ions are lost during the heating step in the sample preparation. Especially chlorine is very sensitive for these losses. HX evaporation could be avoided by using a copper internal standard stable in alkaline conditions. Bromine and iodine could be measured accurate and precise by transforming a simple acidic standard into an alkaline one. Chlorine could be measured by making the same standard but by avoiding the presence of an NH<sub>4</sub>NO<sub>3</sub> matrix.

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### Notes

The authors declare no competing financial interest.

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