

Assuring Traceability of Bromide Measurement in KCl by Ion Chromatography

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ABSTRACT

High purity salts are widely applied in several analytical processes, such as, quality control and preparation of the calibration curves. The metrological control of the purity of these salts is essential to ensure the traceability of analysis based on them. Typically, the contamination of the high purity salts is present in trace levels and the ion chromatography is the most suitable tool for identification and quantification of these contaminants, providing a study of purity of these salts through a sensitive technique, with direct injection, low volume of sample and without the need of pre-concentration. This paper aims to demonstrate traceability of the determination of bromide as impurity in a potassium chloride sample using a validated analytical method through ion chromatography by conductivity suppressor.

1. INTRODUCTION

The potassium chloride is an essential vegetable nutrient used as a fertilizer in combination with other vegetable nutrients. The salt is used in various types of industries, such as inks, soaps, detergents, foodstuffs, pharmaceuticals, as well as raw material for the preparation of other chemical substances such as potassium hydroxide and potassium carbonate. The potassium chloride is an important chemical reagent used in large scale in chemical and pharmaceutical industries for various purposes and the purity required for most of these applications is about 98 % [1].

Inmetro, as the National Metrology Institute (NMI), aims to ensure traceability and greater reliability in purity of salts, promoting the improvement of the quality of products and thus, the competitiveness of Brazilian industries. So, its participation in international comparisons confers international recognition of the results obtained by Inmetro, through its Inorganic Laboratory - LABIN which has participated in a key comparison CCQM – K48, for determining the purity of a KCl sample by ion chromatography together with the Electrochemical Laboratory – LABEL by coulometry.

The sample used for the accuracy tests was a high purity KCl salt also used in a key-comparison organized by the Consultative Committee for Amount of Substance (CCQM), and coordinated by NIM (National Institute of Metrology P. R. China, former NRCCRM) called CCQM-k48. The reference value used is the average of all results submitted by the participating laboratories.

This paper aims to demonstrate traceability of the determination of bromide as impurity in a potassium chloride sample, using a validated analytical method through ion chromatography by conductivity suppressor.

2. EXPERIMENTAL

2.1. Solutions and Reagents

Ultra pure water obtained by an Elix 10 reverse osmosis system a Milli-Q gradient A10 system (Millipore, Bradford, USA) with resistivity of 18.2 M Ω ·cm was used to prepare all solutions.

The calibration solutions of KCl were prepared through the gravimetric dissolution of appropriated masses of the certified reference material SRM 3184 from NIST in ultra pure water in order to prepare the six calibration solutions of concentration (0.05; 0.10; 0.50; 0.70; 1.00 and 1.50) mg·kg⁻¹, respectively. The masses of bromide solutions were weighed in 50 ml capacity PP flasks and completed to approximately 50 g in the same flasks. These solutions were prepared, immediately before analysis.

2.2. Instrumentation

The chromatographic system used was a Dionex Model ICS 2000 equipped with an Ion Pac AS 18 analytical column and an Ion Pac AG 18 precolumn with internal diameter of 5 μ m and dimensions of 4 mm x 250 mm and 4 mm x 50 mm, respectively. These columns were coupled with an ASRS ultra 4mm membrane conductivity suppressor of 99 mA current. A gradient pump device GS 50 was used. Sample injection volumes of 25 μ L were used in a system coupled with an auto sample AS40.

Separation was based on ion exchange chromatography using eluent generator of sodium hydroxide. Conductivity signals were measured by a stabilized conductivity cell DS 6, which was controlled by an electrochemical detection module ED 50.

The chromatograms were obtained with the aid of Chromeleon software version 6.50. Equipment and software were supplied by Dionex (Dionex Corporation, Sunnyvale, USA).

Analytical balance used to prepare all solutions was a Satorius, model ME235S, of 0.01 mg resolution.

2.3. Sample Preparation

The sample from CCQM-k48, denominated in this work as unknown sample and the quality control (QC) sample (SRM 999B) were dried for 6 h at 500 °C without crushing or grinding. After being dried, they were placed in a desiccator with silica gel, and cooled to room temperature before weighing it.

Aliquots of the samples were taken from the bottle to the weighing flask using PTFE coated spatula. Two aliquots of approximately 0.5 g of each sample (unknown and QC) were taken to 50 ml capacity PP flasks for the determination of bromide. The samples were diluted gravimetrically with type-one water to a final mass of about 50 g in the same flask the salts were weighed. The samples were filtered using 0.22 mm Millex filter (Millipore, Brazil) before introduction in chromatographic system by auto-sampler. Sixteen replicates of each aliquot were analyzed. The analyses were performed immediately after dissolution.

3. RESULTS

This work provides an analytical method for the determination of bromide impurity in KCl salt. The best method optimization was obtained by using an eluent flow rate of 1.2 ml·min⁻¹ and eluent composition of 30 mmol·l⁻¹ KOH. In these conditions, the background conductivity obtained in the detector was around 0,55 µS/cm and 224 3 psi system pressure. In Fig. 1, a typical chromatogram of salt sample can be seen using the described optimized conditions. This sample was diluted 100 times prior to analysis due to concentration of chloride, which was extremely high. Neither the resolution nor the efficiency was affected. No sample pretreatment was performed, except for membrane filtration.

3.1. Analytical Features

Analytical curves were obtained in a range between 0.05 mg·kg⁻¹ and 1.5 mg·kg⁻¹ by using six calibration solutions. Correlation coefficient was better than 0.999 6 and sensibility 0.43.

The detection limit (LoD) 0.000 1 µg·kg⁻¹ and quantification limit (LoQ) 0.000 3 µg·kg⁻¹ of the method were obtained from the standard deviation of the curve blank, eight replicates were measured and the LoD was considered to be 3 times the standard deviation (SD) of these replicates, in an analogous approach, the LoQ was considered to be 10 times the SD [2]. The method accuracy was evaluated by the relative deviation of the measurement from a control solution. The average of bromide mass fraction determined in the sample was 31.32 mg·kg⁻¹ with expanded uncertainty of 0.41 mg·kg⁻¹, with coverage factor ($k=2$) and confidence level of 95 %.

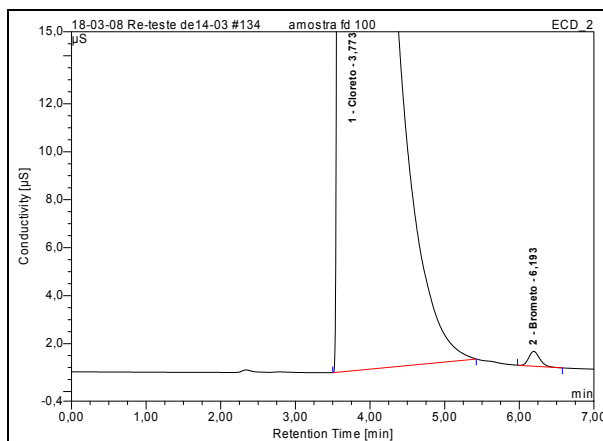


Fig.1. Typical chromatogram obtained from the separation of chloride and bromide in KCl sample. Mobile phase flow rate of 1.2 ml·min⁻¹ and eluent composition of 30 mmol·l⁻¹ KOH.

3.2. Uncertainty Calculation

The uncertainty was estimated based on the EURACHEM [2] and ISO GUM [3], and the sources of uncertainty considered were: the dilution of calibration standards, the repeatability of the equipment, the calibration curve and deviation from control solution, as seen in Table 1.

The uncertainty associated to the repeatability of measurements was obtained from the standard deviation of the pick areas used to determine the bromide concentration in the samples.

Table 1. Results obtained and uncertainty sources.

Uncertainty Sources	
Associated to standard dilution (u(dil)) (relative)	0,004
Associated to repeatability (u(Rep)) (mg·kg ⁻¹)	0,070
Associated to the calibration curve (u(calib)) (mg·kg ⁻¹)	0,134
Deviation from control	0,000
Combined (u(comb)) (mg·kg ⁻¹)	0,205
Coverage Factor (k, 0.05)	2
Expanded (U) (mg·kg ⁻¹)	0.41

4. DISCUSSION

The procedures adopted for preparing calibration solutions and for bromide mass fraction determination in the sample, along with the evaluation of uncertainty taking into account all the relevant sources, assure the traceability of the results of the measurements. Fig. 1 illustrates the main steps to trace the determinations presented on this work to the SI units.

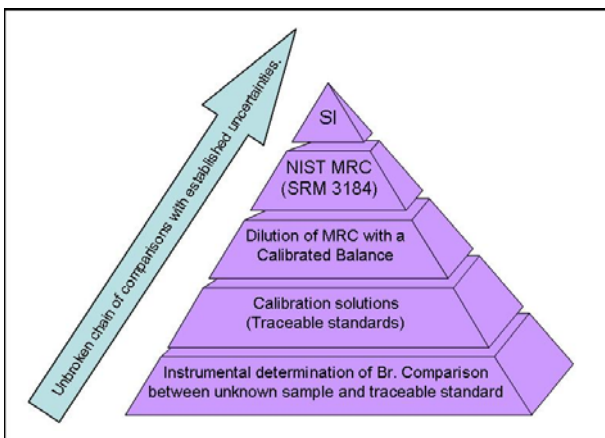


Fig. 2. Establishment of measurement traceability.

The quality control sample (SRM 999b) wasn't included in the traceability chain because the uncertainty showed in the certificate is too large (approximately 35 %) and it's not compatible with the methodology applied. The values were only considered to estimate of accuracy only. The deviation from control mentioned in the uncertainty budget refers to results obtained for an in-house reference material used as second internal QC.

The main uncertainty source was the uncertainty associated to the calibration curve, although it

represents the major contribution, it is within the expected limits, it would represent about 0.5 % of the final result. The authors understand that this is almost the possible limit with the approach used.

The results obtained were submitted to CCQM-K48 "Purity of Potassium Chloride". The overall results for bromide are shown in Table 2 [4]. The results obtained were considered satisfactory by the organizer.

Table 2. Results of participants in CCQM-K48 [4].

Institute	Br				Method
	Value (mol.Kg ⁻¹)	Uncertainty	Value (mg.Kg ⁻¹)	Uncertainty	
BAM	0,00051	10%	41	10%	ICP-MS
INMETRO	0,00039	1.3%	31.32	1.3%	Ion Chromatography
KRISS	0,000417	8%	33.32	8%	Ion Chromatography
NIM	0,0006	11%	48	11%	ICP-MS
NIST	0,00044	11%	35	11%	XRF
NMIJ	0,00048	1.28%	38.6	1.28%	Ion Chromatography
SMU	0,00051	18%	40.8	18%	Ion Chromatography
Average	0,00048		38.3		
RSD		15%		15%	

The authors believe that, although the results were considered satisfactory by the organizers, they might be a little biased. The main source of bias is believed to be the presence of different chemical species of bromide in the salt. A chemical treatment of the sample may be necessary to determine total bromine through ion chromatography. One possible change in sample preparation should be the use of more time for the sample to be equilibrated in solution before analysis. Other approaches should be studied in further works.

The uncertainty of 1.3 %, i.e., 0,41 mg·kg⁻¹, is coherent with the repeatability and other uncertainty sources considered including deviation from certified values of the CRM's used as quality control.

5. CONCLUSIONS

The method validation was successful and the traceability was demonstrated. After validation, the method has shown to be appropriate for determination of bromide in high purity KCl and all the chromatographic parameters were satisfactory for the analysis on this level.

The results obtained were considered satisfactory by the organizer, showing good performance of Inorganic Laboratory from Inmetro-LABIN and competence of measuring with accuracy and reliability.

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