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Determination of metal impurities in pure hydroxides and salts by inductively coupled plasma optical emission spectrometry

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Abstract

A simple analytical method sufficient for the determination of Na, K, Ca, Mg, Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V and Zn at mg kg^{-1} levels in pure NaOH, KOH, NaCl and KCl using the optical emission spectrometry was developed. The results of direct determination with multi-elemental aqueous standards were compared with them obtained by the internal standardisation, by the standard addition methods and with the maximal allowable contents of above-mentioned elements in pure chemicals. The method was shown to be very sensitive and exhibits following limits of detection: Na 0.90, K 3.0, Ca 0.064, Mg 0.026, Al 0.43, B 0.13, Ba 0.015, Cd 0.023, Co 0.056, Cr 0.041, Cu 0.063, Fe 0.060, Li 0.017, Mn 0.035, Mo 0.19, Ni 0.055, Pb 0.39, Sr 0.030, V 0.065 and Zn 0.043 (all in mg kg^{-1}). The method presents a satisfactory precision (relative standard deviation 4–11%), high analytical recoveries, linear responses of at least four orders of magnitude, accuracy and low contamination susceptibility.

Keywords: Inductively coupled plasma optical emission spectrometry (ICP OES); Chloride; Hydroxide; Matrix interference; Internal standardisation

1. Introduction

Due to the development of various high-technology industries over the past years, the demand for ultrapure chemicals, mainly salt and hydroxides of alkaline elements, increased. Consequently, also reliable and sensitive procedures for routine analysis of ultra-trace impurities are needed for those chemicals. Trace elements content occurs from μg kg^{-1} to mg kg^{-1} amounts in real salt samples. These trace element concentrations depend on the degree of purity of salts and is usually specified by a producer [1,2] (Table 1).

Regarding common spectral and non-spectral interferences caused by the matrix, the determination of trace metals in salts and hydroxides using wide-spread techniques as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission or mass spectrometry (ICP OES or ICP MS) is possible only in strongly diluted solutions [3,4]. Such sample dilution worsens analytical possibilities. In order to reach desired concentrations, a pre-treatment step is usually included into analytical procedure. Applications based on extraction and preconcentrating techniques have been developed to separate an interfering matrix prior to an analytical ending. However, these techniques are time and labour consuming, increasing analyse cost and risk of contamination. Grouped separation of trace rare-earth elements for their ICP MS determination in ultrapure salts is reported by Ignatova et al. [5] and Keil et al. [6]. Ferreira et al. presented a separation and pre-concentration of nickel (ng g^{-1}) from saline matrices (alkaline salts of analytical grade and table salt) before using ICP OES [7]. On-line separation and pre-concentration was used before analysis of trace elements in urine [8], haemodialysis solution [8], or seawater [9–14]. Kühn et al. analysed thermal brines. The determination of Na, K, Ca, Mg, Sr, Fe, Mn, Si, B, Zn, Pb, Cd was done with ICP OES. The minor constituents Zn, Pb, Cu, Cd, Cr, Sc, Co, Y, La, Ce, Al were enriched by a matrix separation using the cation exchange resin Chelex100 and after an acidic eluation measured using ICP MS [15]. Worden et al. investigated oilfield formation water with TDS values of up to 230 mg L^{-1}. ICP OES and ICP MS were used [16]. Cassella et al. reported the development of a methodology for the direct determination of vanadium in high saline waters (0.8 mol L^{-1} NaCl) derived from offshore petroleum exploration employing electrothermal atomic absorption spectrometry [17].

Practical choice and usability of analytical methods for the determination of impurities in salts depends on concentration levels of the elements determined. ICP OES is an efficient tech-

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Table 1
Specification of pure salts and hydroxides marketed by Sigma–Aldrich and Spolchemie

Element	NaOH		KOH			NaCl		KCl	
	High grade[b], Spolchemie[c]	71690[a], p.a.,ACS[b], SA[c]	60383[a], p.a., ACS[b], SA[c]	High grade[b], Spolchemie[c]	60371[a], TraceSelect[b], SA[c]	71376[a], BioChemikaUltra[b], SA[c]	38979[a], TraceSelect[b], SA[c]	60128[a], BioChemikaUltra[b], SA[c]	05257[a], TraceSelect[b], SA[c]
	Content of element (mg kg^{-1}) less than								
Na			20	10.00	5			200	50
K	1000	200				50	0.05		
Mg		5	5			5	0.05	10	0.05
Ca	10	5	5	10	1	10	0.1	50	0.1
Ag	1	5	5						
Al	5	5	2	1	0.05	5	0.01	5	0.01
Ba		5	5		1	5	2	10	1
Cd		5	5		0.01	5	0.005	5	0.005
Co		5	5		0.01	5	0.005	5	0.005
Cr		5	5			5	0.01	5	0.01
Cu		5	1		0.01	5	0.005	5	0.005
Fe	5	5	5		0.05	1	0.05	2	0.01
Li		5	5		0.5	5	0.5		
Mn		5	5		0.05	5	0.01	5	0.01
Mo		5	5			5		5	
Ni	1	5	1		0.01	5	0.01	5	0.005
Pb			1		0.01	5	0.005	5	0.01
Sr		5	5		0.5	5	0.1		
Zn		5	5		0.05	5	0.005	5	0.005
HM[d]	10			5					

[a] No.
[b] Purity.
[c] Producer/Seller.
[d] HM, the total content of heavy metals; SA, Sigma–Aldrich.

nique for rapid multi-element analysis of a wide scale of various sample types. The suitable choice of nebulizer type together with using of humidifier can overcome possible blockage of the nebulizer orifice. If the saline matrix is simple and known, spectral interferences are easily predicated from the spectral line library. For higher salt concentration in the sample, matrix effect can occur: in case of ICP OES technique it leads mostly to suppression of analytical signal intensity and less commonly to its enhancement. Matrix effects are connected with significant differences in physical properties between calibration standards and analysed samples or are related to changes in the plasma [2]. Methods commonly used for matrix effect elimination are empirical. A sample dilution is not always appropriate because decreases the ICP OES detection ability. In the case of the matrix matching, the real composition of sample matrix is modelled in calibration standards [18]. The standard addition method and the internal standardisation are the mostly used correction and successful technique [19,20]. For correction of drift and matrix effect in ICP OES, Al-Ammar and Barnes [21] developed a modification of internal standardisation based on simultaneous measurement of two different spectral lines of the same analyte.

Extraction techniques, excitation-buffering techniques or mathematical corrections can be also use [8,22,23], but all these techniques have limitations as discussed by Thompson and Ramsay [24]. Mermet [25] reported that matrix effect could be substantially minimized by applying robust operation condition.

The presented work deals with the determination of impurities in pure NaCl, KCl, NaOH and KOH. Specifically, this study has two main objectives: (i) to demonstrate the general advantages of ICP OES in inorganic routine analysis of high saline samples; (ii) to apply the developed methodology to trace elements determinations in several ultrapure products with various guaranteed specification.

2. Experimental

The measurement was carried out with the sequential, radially viewed ICP atomic emission spectrometer INTEGRA XL 2 (GBC, Dandenong Australia; http://www.gbcsci.com), equipped with a ceramic V-groove nebulizer (Glass expansion, Australia; http://www.geicp.com) and a glass cyclonic spray chamber (Glass expansion, Australia; http://www.geicp.com).

Two brands of NaOH and KOH were used in the study: purity "high grade" made by Spolchemie (Spolek pro chemickou a hutní výrobu, Czech Republic; http://spolchemie.cz) and "pro analyses" made by Lachema (Brno, Czech Republic). Both NaCl and KCl analysed were of purity "pro analyses", made by Lachema (Brno, Czech Republic).

The demineralised water was taken from a Milli-Q Plus water-purification system (Millipore, Bedford, USA; http://www.millipore.com).

The single component standards of Na, K, Ca, Mg, Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V Zn, Be, Y and Sc were used ($1000 \pm 3\ \mu g\ mL^{-1}$, CPI International, USA; http://www.cpiinternational.com).

Calibration standards: single and multi-element standards were prepared containing four levels of concentration: single Li 0.5–0.1–0.05–0.025 mg L^{-1}, single K 200–100–50–10 mg L^{-1}, single Na 100–50–20–10 mg L^{-1}, multi-element (i) Al 0.5; Sr and Ba 0.05; B, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, V and Zn 0.5 mg L^{-1}; (ii) the same elements with half concentrations as (i); (iii) the same elements five time diluted as (i); (iv) the same elements 10-fold diluted as (i). All standards were stabilised with 1 mL 65% (w/v) HNO_3/100 mL of solution. As well a standard blank containing 1 mL HNO_3/100 mL was prepared. In concentration given below, internal standards were also added. In case of Li standards, only Be and Y internal standards were used.

Table 2
The operating conditions for ICP OES analysis

RF power	1200 W
View height	5 mm
Gas	Ar 99.999%
Plasma gas	0.7 L min^{-1}
Auxilliary gas	12 L min^{-1}
Nebulizer gas	0.65 L min^{-1}
Sample aspiration rate	2 mL min^{-1}
Read	On-peak, 3 s
Background correction	Fixed point
Number of replicates	3

Internal standardisation: internal standards Be 0.1 mg L^{-1} and Y, Sc 1 mg L^{-1} were used and added individually to each analysed solution during preparation before run.

Standard additions: approximately, 10 g of pure salt sample was accurately weighed into a 100 mL volumetric flask, and 50, 25 and 10 mL of the most concentrated aqueous standard was added.

Sample preparation: 10% solution of salt or hydroxide in demineralised water was used. Internal standards were also added.

The ICP OES method: the measurement conditions were optimised based on signal-to-background ratio of the least sensitive elements (Al and Pb), but it was necessary to modify them in order to set the plasma stable. The measurement conditions and emission lines are listed in Tables 2 and 3. The analyte emission was based on the difference of measured emission intensity on the top of the peak and background near the peak. All detection limits given by ICP OES software were based on triple of standard deviation of the background counts. Including the washing time between samples, the total time for analysis was approximately 5 min.

3. Results and discussion

3.1. Analytical characteristics and process validation

All limits of detection given by ICP OES software were calculated as the concentration equivalent to triple of standard deviation of the background counts (3σ, in $\mu g\ L^{-1}$). The procedural limits of detection (LOD, in mg g^{-1}) were worked out as $LOD = f_{dilution} \times 3\sigma$. The dilution factor $f_{dilution}$ takes into account the dilution of sample during the preparation step. The 3σ were determined by 10 replicates of the lowest calibration

Table 3
Analytical characteristics of ICP OES method

	λ (nm)	LOD (mg kg^{-1})	R.S.D. (%)	$AL_{p.a.}$ (mg kg^{-1})	$AL_{TraceSelect}$ (mg kg^{-1})
Na	588.995	0.902	8.96	<20	<5[c]
K	769.896	2.96	10.6	<50[a]	<0.05
Ca	422.673	0.0636	5.34	<5	<0.1
Mg	285.213	0.0257	4.67	<5	<0.05
Al	167.081	0.427	10.6	<2	<0.01
B	249.773	0.127	6.13		
Ba	455.403	0.0153	5.11	<5	<1[c]
Cd	228.802	0.0232	7.09	<5	<0.005
Co	228.616	0.0562	6.12	<5	<0.005
Cr	267.716	0.0412	4.86	<5	<0.01
Cu	324.754	0.0632	5.13	<1	<0.005[b]
Fe	259.940	0.0600	4.86	<2[b]	<0.01[d]
Li	670.784	0.0169	4.52	<5	<0.5
Mn	257.610	0.0347	6.25	<5	<0.01
Mo	281.615	0.189	7.33	<5	
Ni	221.647	0.0549	4.28	<1	<0.005[d]
Pb	220.353	0.489	8.19	<1	<0.005
Sr	407.771	0.0299	6.83	<5	<0.1
V	311.071	0.0651	7.23	<5	
Zn	213.856	0.0428	4.82	<5	<0.005

LOD, limit of detection; R.S.D., relative standard deviation; $AL_{p.a.}$, acceptable limit for impurities in KOH (p.a., ACS); $AL_{TraceSelect}$, acceptable limit for impurities in NaCl (TraceSelect); NaOH (p.a., ACS).
[a] NaCl (BioChemicaUltra).
[b] KCl (BioChemikaUltra).
[c] KOH (TraceSelect).
[d] KCl (TraceSelect); data obtained on web [1].

standard measurements with the presence of 10% NaOH. Mainly in the case of Mg, Ca and Ba, it was necessary to reduce the photo-multiplier voltage to lower their signal intensities. So, the real ICP OES detection ability for Mg, Ca and Ba is much better. They are summarised in Table 3. In Fig. 1, the comparison of procedural LODs and acceptable limits for purities "pro analyses" ($AL_{p.a.}$) and "TraceSelect" (AL_{TS}) is displayed. Evidently in cases of all elements, the procedural LODs are lower than $Al_{p.a}$. The method is also convenient for the determination of Na, Ca, Mg, Ba, Li and Sr because AL_{TS} are higher than LODs.

3.2. Analysis of spiked samples

Before the analysis of spiked samples, the standard addition method was carried out in order to find out real concentrations of elements analysed. Cd, Co, Cr, Cu, Li, Ni, Mo and V were found to be below limits of detection in all samples analysed. For other elements, readable concentration were found and counted up to spiked amounts. Without any matrix effect correction, the direct analysis of Na, K, Ca, Mg, Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V and Zn was carried out for spiked samples of 10% solutions of NaOH, KOH, NaCl and KCl (all samples were of "pro analysis" purity). For these experiments, following internal standards were used: Be 313.107 nm, Y 322.789 nm and Sc 356.770 nm. Sc was not used as the internal standard for Li due to a spectral interference.

It is clear from the results given in Fig. 2 that determinations using direct calibration with aqueous standard do not provide good results because recoveries vary between 60 and 95% depending on element analysed and matrices. The internal standard Be put up satisfactory recovery from 92 to 102%.

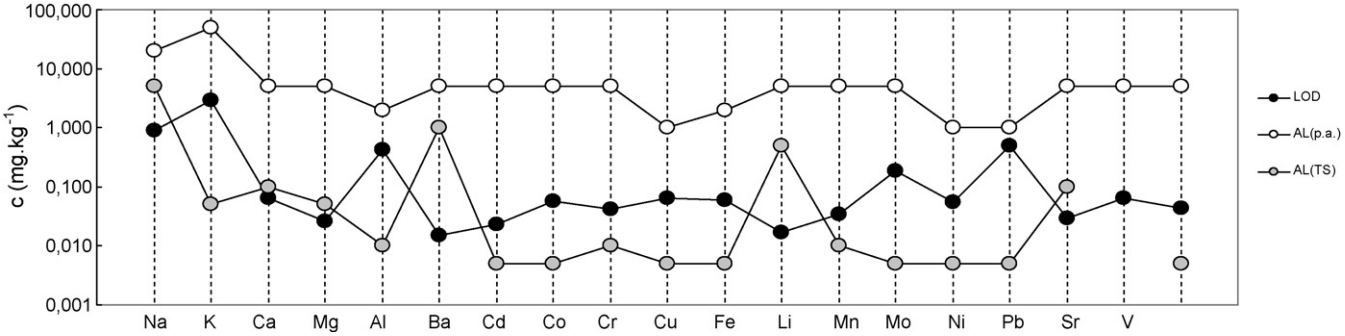

Fig. 1. Comparison of the procedural limits of detection with acceptable limits for purity "pro analyse" and "TraceSelect". LOD, the procedural limit of detection, AL(p.a.), acceptable limit for purity "pro analyse" AL(TS) acceptable limits for purity "TraceSelect".

Table 4
Results of ICP OES analysis of 10% solution of NaOH, KOH, NaCl and KCl

Method	Chemical/Element (mg kg^{-1})	Na	K	Ca	Mg	Al	B	Ba	Fe	Mn	Pb	Sr	Zn
No IS			64.3	0.0813	0.0526	0.778	0.226	0.0176	0.0878	0.0607	<LOD	0.0300	0.0464
IS Be	NaOH (p.a.)		68.1	0.0807	0.0733	0.914	0.286	0.0202	0.0932	0.0708		0.0310	0.0600
SA			65.8	0.0831	0.0756	0.990	0.290	0.0213	0.0976	0.0747		0.0334	0.0612
No IS			27.3	0.0719	0.0286		0.104	0.0148	0.064			0.027	
IS Be	NaOH (h.g.)		37.3	0.0714	0.0287	<LOD	0.127	0.0167	0.0693	<LOD	<LOD	0.0297	<LOD
SA			27.6	0.0735	0.0296		0.134	0.0172	0.0711			0.0313	
No IS		96.7		0.299	0.0416	0.474	0.406	0.0309	0.121	0.0433	<LOD	0.405	0.0973
IS Be	KOH (p.a.)	93.9		0.303	0.0418	0.572	0.495	0.0339	0.136	0.0504		0.0481	0.121
SA		98.5		0.310	0.0421	0.598	0.509	0.0353	0.135	0.0522		0.0484	0.124
No IS		21.7		0.0895	0.0319		0.171	0.0172	0.0883			0.028	<LOD
IS Be	KOH (h.g.)	21.7		0.0909	0.0321	<LOD	0.209	0.0207	0.108	<LOD	<LOD	0.0333	<LOD
SA		21.3		0.0926	0.0323		0.215	0.0214	0.0982			0.0335	<LOD
No IS			29.3	0.0879	0.0591		0.182	0.0148	0.0743			0.249	0.0793
IS Be	NaCl (p.a.)		29.8	0.0887	0.0619	<LOD	0.226	0.0179	0.0821	<LOD	<LOD	0.0292	0.0984
SA			30.70	0.0913	0.0623		0.233	0.0185	0.0830			0.0302	0.0726
No IS		48.6		0.641	0.0808	0.545	0.212	0.0586	0.0926		4.82	0.0689	0.0782
IS Be	KCl (p.a.)	51.1		0.647	0.0838	0.635	0.248	0.0677	0.0996	<LOD	5.56	0.0799	0.0979
SA		50.5		0.666	0.0852	0.645	0.256	0.0699	0.103		5.68	0.0833	0.0993

No IS, no internal standard; IS Be, the internal standard Be 313.107 nm; SA, the standard addition method; Cd, Co, Cr, Cu, Li, Ni, Mo, V < LOD.

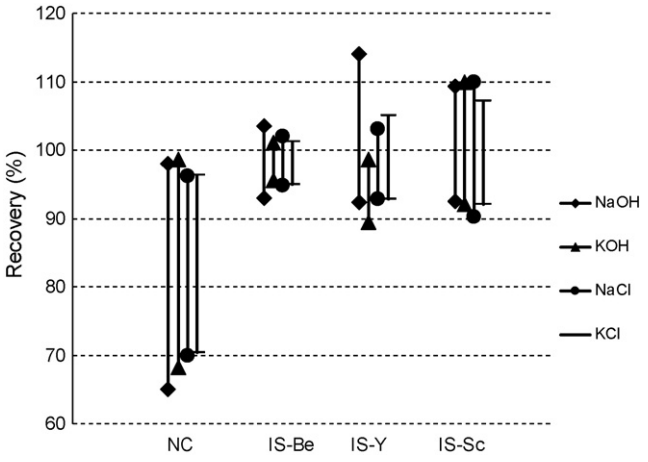

Fig. 2. Analysis of spiked 10% NaOH, KOH, NaCl and KCl. Recoveries for the determination without matrix effect correction and for the internal standardisation with Be, Y and Sc are compared. NC, non-correction; IS-Be, internal standard Be; IS-Y, internal standard Y; IS-Sc, internal standard Sc.

For Sc and Y, recoveries vary from 92 to 110% and from 90 to 114%, respectively. Based on comparison of results of internal standard, Be can be recommended as the best internal standard. It was thus used for matrix effect correction.

3.3. Analysis of NaOH, KOH, NaCl and KCl samples

Using the standard addition method and the internal standardisation with Be, samples of 10% solutions of NaOH, KOH, NaCl and KCl (substances were of "high grade" and/or "pro analysis" purity) were analysed for Na, K, Ca, Mg, Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V and Zn. Above-mentioned procedures were compared also with direct determination without correction of matrix effect. All results are summarised in Table 4. In case of Cd, Co, Cr, Cu, Li, Ni, Mo and V, no detectable amount was found.

4. Conclusion

A simple internal standardisation technique has been utilised for multi-element analysis of Na, K, Ca, Mg, Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V and Zn in 10% water solutions of pure NaOH, KOH, NaCl and KCl using ICP OES. In comparison with more time consuming standard addition method, the results obtained for the internal standard Be are comparable. Expectably, results obtained for the ICP OES analysis without any correction of the saline matrix effect are significantly lower (tens of percent) and unusable for routine analysis. In all cases of analysed samples, Cd, Co, Cr, Cu, Li, Ni, Mo and V were not detected. Regrettably, the determined average levels of the elements in the analysed sample cannot be related to producer specifications. According to the information available on web pages [1], Sigma–Aldrich guarantee maximal impurity amounts in discussed salt as given in Table 1. The procedural limits of detection of proposed method obtained are deeply below the acceptable limits specified for purity "pro analyses" as well as amount determined in analysed salt (Table 3, Fig. 1). The method is also convenient for determination of Na, Ca, Mg, Ba, Li and Sr because AL_{TS} are higher than LODs.

The proposed analytical method offers an interesting perspective for elemental analysis of impurities in other similar pure materials or highly saline matrices. It enables to avoid a time and labour-consuming separation pre-treatment step, decreases analyse cost and risk of contamination and simplifies laboratory work.

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