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Determination of metal impurities in ultrapure $CaCl_2$ and $MgCl_2$ by ICP OES

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Abstract. An effective, rapid and simple analytical method for the determination of Na, K, Ca, Mg, Cd, Pb, Ba, Fe, Mn, Sr, Zr, Cu, Zn and Al at mg kg^{-1} levels in the ultrapure salts $MgCl_2$ and $CaCl_2$ using optical emission spectrometry was developed. Optimisation of the operation conditions was performed with real samples of ultrapure $MgCl_2$ and $CaCl_2$. The results of the determination with multi-elemental water standards were compared to the internal standardisation, the standard addition method, and the maximum allowable content of the above mentioned elements in pure chemicals. The method was shown to be very sensitive with the following limits of detection: Na 1.01, K 3.12, Ca 0.263, Mg 0.275, Cd 0.0832, Pb 0.482, Ba 0.0153, Fe 0.0528, Mn 0.0473, Sr 0.0203, Zr 0.638, Cu 0.0732, Zn 0.0686 and Al 0.459 (all in mg kg^{-1}). The method exhibited satisfactory precision, high analytical recoveries, linear responses of an accuracy of at least 4 orders of magnitude and low contamination susceptibility.

Key words: ICP OES, $MgCl_2$, $CaCl_2$, matrix interference.

Since over the past years various high-technology industries have increased their demand for ultrapure chemicals, mainly salts of alkaline and alkaline earth elements, reliable and sensitive procedures for routine analysis of ultra-trace impurities are required for these chemicals. Trace elements occur from μg kg^{-1} to mg kg^{-1} amounts in real salt samples. The amount of the element depends on the degree of purity of the salts and is usually specified by the producer (Table 1) [1].

Regarding common spectral and non-spectral interferences caused by the matrix, determination of trace concentration of metals in salts using common techniques such as AAS, ICP OES or ICP MS is possible only in strongly diluted salt solutions [2, 3]. Sample dilution worsens the detection limits. In order to reach the desired detection limits, a pre-treatment step is usually included in the analytical procedure. Applications based on extraction and preconcentration techniques have been developed to separate the interfering matrix prior to analysis. Group separation of trace rare-earth elements for their ICP MS determination in high-purity calcium chloride has been reported by Ignatova et al. [4] and Keil et al. [5]. They separated trace metal impurities in ultrapure inorganic salts before high resolution ICP MS analysis. On-line separation and preconcentration was used prior to analysis of the trace elements in urine [6] or sea water [7]. However, these techniques are time-consuming and labour-intensive, costly and pose the risk of contamination.

The practical choice and usability of analytical methods for the determination of impurities in salts depends on the concentration levels of the elements determined. ICP OES is an efficient technique for rapid multi-element analysis of a wide scale of various

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Table 1. Specification of pure salts marketed by Sigma-Aldrich

	Al	Ba	Ca	Cd	Cu	Fe	K	Mg	Na	Pb	Sr	Zn	HM[a]
$CaCl_2 \cdot 2H_2O$	*Content of element [mg kg^{-1}] less than:*												
23506 ACS		50				10	100	50	200		1000		5
21100 p.a.				50		10	100		500	50			
12022 pharm.	1					10	100	500	200	5			
$MgCl_2 \cdot 6H_2O$	*Content of element [mg kg^{-1}] less than:*												
13152 pharm.	1	20	1000		10	5	5000		5000	10		10	
9272 ACS		50		50		5	50		50				50

[a] *HM* Heavy metals.

sample types. The suitable choice of a nebulizer type together with a humidifier can overcome possible blockages in the nebulizer orifice. If the saline matrix is simple and known, as in the case of $MgCl_2$ and $CaCl_2$, the spectral interferences are easily predicated from the spectral line library. For higher salt concentrations in the sample, the matrix produces non-spectral interferences that in ICP OES lead mostly to the suppression of the analytical signal intensity and less commonly to its enhancement. Matrix effects are connected with significant differences in the physical properties of calibration standards and analysed samples or are related to changes in plasma [2].

Matrix effects must be considered in the impurities determination. All methods commonly used for matrix effect elimination are empirical. One of the simple procedures is the matrix matching: the practical composition of the sample matrix is modelled in calibration standards [8]. The simple sample dilution is not appropriate because it decreases ICP OES detection ability [9]. The standard addition method and the internal standardisation are the most frequently used correction and a successful technique [8, 10]. For correction of drift and matrix effects in ICP OES, Al-Ammar and Barnes [11] 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 also be used [12–14], but all these techniques have limitations, as discussed by Thompson and Ramsay [15]. Mermet [16] reported that the matrix effect can be substantially minimized by applying robust operation conditions.

The present study reports the results of determination of impurities in ultrapure $MgCl_2$ and $CaCl_2$. 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 methodology to trace metals of several ultrapure products with different guaranteed specification.

Experimental

Measurements were carried out with the sequential, radially viewed ICP atomic emission spectrometer INTEGRA XL 2 (GBC, Dandenong Australia; 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).

Three brands of $CaCl_2$ and $MgCl_2$, "ACS" purity and "pharmaceutical" made by Macco Organiques (Bruntál, Czech Republic) and "pro analyses" made by Lachema (Brno, Czech republic), were used in the study.

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

Single component standards of Ca, Mg, K, Na, Cd, Pb, Ba, Fe, Mn, Zr, Sr, Cu, Zn, Al, Be, Y, Sc, Ga, Tl were used ($1000 \pm 3\,\mu g\,mL^{-1}$, CPI International, USA; http://www.cpiinternational.com).

Calibration standards

Three multi-element standards were prepared containing (i) Cd, Zr, Cu, Zn, Al ($1\,mg\,L^{-1}$), Fe, Mn, Pb ($2\,mg\,L^{-1}$), Sr, Ba ($5\,mg\,L^{-1}$), Na, K ($50\,mg\,L^{-1}$), (ii) the same elements with half the concentrations as (i), (iii) the same elements in ten-fold dilution of (i). Single element standards of Mg and Ca containing 50, 25 and $5\,mg\,L^{-1}$ were used. All standards were stabilised with 1 mL 65% w/v HNO_3/100 mL of solution. Additionally, a standard blank containing 1 mL HNO_3/100 mL was prepared. To the concentration given below, internal standards were also added.

Table 2. Operating conditions for ICP OES analysis

RF power	1100 W	nebulizer gas	$0.65\,L\,min^{-1}$
View height	5 mm	sample aspiration rate	$2\,mL\,min^{-1}$
Gas	argon99.999%	read	on-peak, 3 s
Plasma gas	$0.6\,L\,min^{-1}$	background correction	fixed point correction
Auxiliary gas	$10\,L\,min^{-1}$	number of replicates	3

Table 3. Analytical characteristics of the ICP OES method

	λ [nm]	LOD [mg kg^{-1}]	RSD [%]	AL [mg kg^{-1}]		λ [nm]	LOD [mg kg^{-1}]	RSD [%]	AL [mg kg^{-1}]
Na	588.995	1.01	9.11	<50	Cu	324.754	0.0732	6.23	<10[a]
K	769.896	3.12	15.6	<50	Fe	259.940	0.0528	4.18	<5
Ca	422.673	0.263	5.43	<100	Mn	257.610	0.0473	5.26	<5
Mg	285.213	0.275	4.46	<500[a]	Sr	407.771	0.0203	6.18	<50
Al	167.081	0.459	12.6	<1[a]	Pb	220.353	0.482	9.82	<5[a]
Ba	455.403	0.0153	5.71	<50	Zn	213.856	0.0686	5.12	<10[a]
Cd	228.802	0.0832	6.22	<50[b]	Zr	339.198	0.0638	6.03	

LOD Limit of detection, *RSD* relative standard deviation, *AL* acceptable limit for impurities in $MgCl_2 \cdot 6H_2O$ (“ACS”).
[a] $MgCl_2 \cdot 6H_2O$ (“pharm.”), [b] $CaCl_2 \cdot 2H_2O$ (“pharm.”); data obtained on Web [7].

Internal standardisation

Internal standards Be (0.1 mg L^{-1}) Y, Sc (1 mg L^{-1}), Ga, Bi, Tl (10 mg L^{-1}) were used.

Standard additions: a sample of approximately 10 g of pure salt was accurately weighed into a 100 mL volumetric flask, and 50, 25 and 10 mL of the most concentrated aqueous standard and 1 mL HNO_3/100 mL was added.

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

The ICP OES method

The measurement conditions were optimised based on the signal-to-background ratio of the least concentrated elements (Al, Pb). The measurement conditions and emission lines are listed in Tables 2 and 3. The analyte emission was based on taking the difference of the measured emission intensity at the top of the peak and background near the peak. In all cases, aqueous calibration standards were used. All detection limits given by the ICP OES software were based on three times the standard deviation of the background counts. Including the washing time in between samples, the total time for analysis was approximately 5 minutes.

Results and discussion

Analytical characteristics and validation of the process

All limits of detection given by the ICP OES software were calculated as the concentration equivalent to three times the standard deviation of the background counts (3σ, in μg L^{-1}). The procedural limits of detection (LOD, in mg g^{-1}) were worked out as $\mathrm{LOD} = f_{\mathrm{dilution}} * 3\sigma$. The dilution factor f_{dilution} takes into account the dilution of the sample during the preparation step. The 3σ were determined by ten-fold measurements of the lowest calibration standards of the different elements. The determined limits of detection and relative standard deviations are summarised in Table 3.

Analysis of spiked samples

Without any matrix effect correction, direct analysis of Cd, Pb, Ba, Fe, Mn, Sr, Zr, Cu, Zn and Al was carried out for spiked samples of 10% solutions of $CaCl_2$ and $MgCl_2$ (both samples were of “ACS” purity). Also, various internal standards were used: Be 313.107 nm, Y 322.789 nm, Sc 356.770 nm, Ga 417.206 nm, Bi 306.772 nm, Tl 351.924 nm and Ar 419.832 nm. From the results given in Table 4 it is clear that the internal standard Be and in most cases Sc provided satisfactory recovery. Depending on the element analysed, recoveries ranged between 70 and 95% for other internal standards tested. In the case of Sr, Ba and Zn, some amount of these elements is presented in the samples used.

Table 4. Results of ICP OES analysis of spiked samples of 10% solution of $CaCl_2$ and $MgCl_2$ (both “ACS” purity)

Internal standard	Salt	Found [mg L^{-1}]									
		Al	Ba	Cd	Cu	Fe	Mn	Sr	Pb	Zn	Zr
		Spiked [mg L^{-1}]									
		1.00	5.00	1.00	1.00	2.00	2.00	5.00	2.00	1.00	1.00
No internal std.	$CaCl_2$	0.46	3.64	0.72	0.82	1.16	1.08	7.60	1.04	1.00	0.65
Be 313.107 nm		0.98	5.40	1.00	1.01	1.97	1.97	10.1	1.92	1.08	1.09
Sc 356.770 nm		0.95	5.04	1.01	0.98	1.49	1.51	9.94	1.98	1.03	0.84
No internal std.	$MgCl_2$	0.58	3.85	2.28	0.81	1.36	1.27	3.68	1.19	1.02	0.74
Be 313.107 nm		0.93	5.10	1.04	1.00	1.88	1.93	5.75	1.87	1.02	1.09
Sc 356.770 nm		0.98	5.04	0.98	1.03	1.77	1.78	5.14	1.97	1.06	0.99

Table 5. Analysis of $CaCl_2$ and $MgCl_2$ by means of ICP OES without matrix effect correction and using the internal standard beryllium and the standard addition technique

Sample	Method	Na	K	Mg	Ca	Ba	Cu	Fe	Sr	Zn	Mn, Cd, Pb, Zr, Al
		[mg kg^{-1}]									
$CaCl_2$ "ACS"	NC	17.0	38.7	21.9		1.21	<LOD	0.121	3.12	0.119	<LOD
	IS Be	23.3	25.9	30.7		1.94		0.147	5.80	0.149	
	SA	22.7	25.5	33.2		2.04		0.130	5.75	0.155	
$CaCl_2$ "pharm."	NC	32.3	41.1	92.5		0.832	0.0827	0.112	4.23	0.0601	
	IS Be	46.7	43.3	134		1.50	0.143	0.135	7.83	0.0580	
	SA	46.3	41.1	138		3.31	0.136	0.099	7.12	0.0548	
$CaCl_2$ "p.a."	NC	24.8	5.44	3.47		0.123	0.0815	0.0513	4.16	0.0107	
	IS Be	35.8	12.8	5.07		0.409	0.113	0.158	5.30	0.0160	
	SA	35.2	12.7	5.07		0.580	0.110	0.190	5.39	0.0144	
$MgCl_2$ "ACS"	NC	29.5	55.6		14.1	0.081	<LOD	<LOD	<LOD	0.104	
	IS Be	44.8	64.9		23.3	0.108			0.06	0.131	
	SA	48.2	63.8		21.1	0.321			0.06	0.141	
$MgCl_2$ "pharm."	NC	5.11	103		197	0.302	0.089	<LOD	0.32	0.0102	
	IS Be	7.38	151		239	0.896	0.151	0.380	0.50	0.0152	
	SA	7.38	150		222	1.06	0.169	0.404	0.46	0.0164	
$MgCl_2$ "p.a."	NC	0.90	40.2		1.02	<LOD	0.086	0.528	0.02	0.0641	
	IS Be	1.86	61.3		1.33		0.201	1.17	0.08	0.0750	
	SA	1.78	61.4		1.36		0.201	1.17	0.09	0.0725	

NC Non correction, *IS Be* the internal standard beryllium, *SA* the standard addition technique.

Analysis of $CaCl_2$ and $MgCl_2$ samples

Using the standard addition method and the internal standardisation with Be, samples of 10% solutions of $CaCl_2$ and $MgCl_2$ (both salts were of "ACS" purity, "pharmaceutical" and "pro analysis") were analysed for Cd, Pb, Ba, Fe, Mn, Sr, Zr, Cu, Zn, Al, Na, K, Mg and Ca. The above mentioned procedures were compared with direct determination without correction of matrix effect. All results are summarised in Table 5.

Conclusion

A simple internal standardisation technique has been utilised for multi-element analysis of Cd, Pb, Ba, Fe, Mn, Sr, Zr, Cu, Zn, Al, Na, K, Mg and Ca in 10% water solutions of pure $CaCl_2$ and $MgCl_2$ salts using ICP OES. Compared to the more time-consuming standard addition method, the results obtained are compatible. Expectably, the results obtained for the ICP OES analysis without any correction of the saline matrix effect are significantly lower (tens of percent) and unusable in routine analysis. In none of the cases of the analysed samples Cd, Pb, Mn, Zr or Al were detected. Regrettably, the average determined levels of the elements in the analysed sample cannot be related to the producer specifications. According to the information available on web pages [1], Sigma Aldrich guarantee maximum impurity amounts in the salt discussed, as given in Table 1. The limits of detection obtained with the proposed method are far below these data as is the amount determined in the analysed salt (Tables 3, 5).

The proposed analytical method offers an interesting perspective for elemental analysis of impurities in other, similar ultrapure materials. It avoids the time-consuming and labour-intensive separation pre-treatment step, decreases analysis costs and the risk of contamination, and simplifies laboratory work.

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