

Comparison of methods used for elimination of matrix effect in ICP-AES

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Abstract The determination of Al, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V and Zn in high-saline solutions (urine) by ICP-AES method has been studied. The interference due to individual components (NaCl, KCl, CaCO₃, MgCl₂, NH₄H₂PO₄, HCl, H₂SO₄ and urea) and their concentration levels were evaluated. Suppression of down to 20 % of trace element content was found due to the main inorganic components of urine. The methods for correction of matrix effect, i.e. internal standardisation with Y, Sc and Ar, the “CAIS” technique and determination under robust condition were tested and compared with the results of direct determination. The organic components of urine had no significant effect. Two approaches of estimation of LOD were used. The influence of urine matrix on LOD was established. Precision (RSD) was about 1% for internal standardisation and less than 2% for direct estimation. The accuracy was evaluated with urine control materials SeronomTM Trace Element Urine, batch 403125 (Nycomed Pharma), and Lypocheck 69012 (Bio-Rad).

Key words: Trace elements, ICP-AES, Urine, Matrix Effect, Internal Standardisation.

1. Introduction

Determination of major and trace elements in urine has been used in connection with metabolic balance studies, as a therapeutic monitor in the treatment of disease, as a diagnostic tool in clinical chemistry, and in the evaluation of occupational or environmental exposure to metals. Different methods have been employed for the determination of elements in urine.

Practical choice and usability of analytical methods depend on concentration levels of the elements determined. Trace elements occur from “ppb” to “ppm” amounts in real urine samples. The widely extended and practically used analytical methods are ET-AAS. Due to the necessity of a specialised operator and considerable working expenses, ICP-MS and NAA are not used in routine biochemical service. ICP-AES is an efficient technique for rapid multi-element analysis of a wide scale of various sample types. One of the disadvantages of ICP-AES is a detection limit higher than the physiologically occurring trace element amounts in urine in some cases. Nevertheless, ICP-AES is suitable for over-critical concentrations, which indicate anomalous body condition [1, 2].

Urine has a complex constitution and exhibits great variation in matrix elements [3-5]. The matrix composition and especially considerable versatility of urine samples influence not only results of direct ICP-AES estimation of trace elements but they cause problems in other methods. Na and K, which are easily ionised elements (EIE), cause matrix interference in inductively coupled plasma atomic emission spectrometry. Several effects due to these easily ionised elements in ICP-AES are reported in special literature. Non-spectral interferences in ICP-AES lead mostly to suppression of analytical signal intensity and less commonly to its enhancement [6-9].

Matrix effects are connected with significant differences in the physical properties of the calibration standards and analysed sample or are related to changes in plasma (e.g. excess of electrons from the matrix). Matrix effect must be considered in common analytical practice. Owing to the matrix effect, a description by an integral theory is practically impossible: all the methods used for matrix effect elimination are empirical [10-11].

There is a wide scale of correction techniques. One of simple procedures is matrix matching: the practical composition of sample matrix is modelled in calibration standards [12]. Unfortunately, this procedure is not suitable in case of trace element analysis of urine due to substantial matrix variability. A simple sample dilution is not appropriate too. A sample dilution decreases the urine trace elements below the ICP-AES detection ability [13].

When the former is not applicable, several other techniques can be used to correct for matrix effects. The standard addition method rises the time and expenses required for the analysis. The internal standardisation is the mostly used correction technique although its disadvantage is similar as in the case of standard addition [12, 14]. Al-Ammar and Barnes developed an original common analyte internal standardisation (CAIS) technique to correct for drift in ICP-AES [15].

However, they also used it to correct matrix effect, and this seems to offer a new view of correction methods. The CAIS technique is based on simultaneous measurement of two different spectral lines of the same analyte. One of the lines is used as a measure for the concentration (analyte line) and the other line as internal reference for matrix effect correction. No addition of internal standard is necessary in this technique. The CAIS requires that the analyte line intensity to be affected by matrix in a way different from that of the internal reference line intensity [16].

Other methods could also be used: extraction techniques leading to removal of the matrix, excitation-buffering techniques or mathematical correction by curve fitting to an empirical function [17-19]. All these techniques have limitations as discussed by Thompson and Ramsay [20].

Mermet [21] reported that matrix effect can be substantially minimized by applying robust operation condition, i.e. a low nebulizer gas flow and a high rf power level. Robust plasma conditions are described by the intensity ratio of the Mg II 280.270 nm line with respect to the Mg I 285.213 nm. This Mg II/I line ratio can be defined to evaluate the analysis robustness respecting the matrix effect, and can also be used as a fast diagnostic tool in the control of ICP systems [22]. Similar recommendations are also given by other authors [23, 24].

The aim of this work is to describe the influence of matrix elements on determination of trace elements in urine and to develop a practical and efficient method to correct matrix effect of EIE. The efficiency of chosen correction methods is compared in the study presented.

Experimental

Instrumentation

The measurement was carried out with the ICP atomic emission spectrometer “Integra XL 2” from GBC, Australia. The used emission lines are listed in Table 1; the measuring parameters are listed in Table 2.

Table 1 Emission lines and background correction

Element	λ [nm]	Order	BC [nm]	Element	λ [nm]	Order	BC [nm]
Al I	308.215	2	± 0.0160	Ni II	221.647	2	± 0.0310
Be I	234.861	2	± 0.0180	Zn I	213.856	3	± 0.0080
Cd I	228.802	3	± 0.0085	Pb I	216.999	3	± 0.0125
Co II	228.616	2	± 0.0165	V II	309.311	1	+ 0.0500
Cu I	324.754	1	± 0.0300	Y II	371.030	1	± 0.0393
Cr I	357.869	1	± 0.0320	Ar I	727.294	1	Dynamic
Mn I	403.071	1	± 0.0270	Sc II	357.253	1	± 0.0320

λ [nm] – wavelength, I – atomic line, II – ion line, BC – background correction

Table 2 Device and measuring parameters

Parameter	Value	Parameter	Value
Plasma power supply*	1.0 kW	Photomultiplier voltage	600 V
Observation height	6 mm	Sample uptake rate	1.7 mL min ⁻¹
Plasma gas flow*	10.0 L min ⁻¹	Integration time	1.0 s
Auxiliary gas flow	0.50 L min ⁻¹	Sample time delay	30.0 s
Nebulizer gas flow	0.60 L min ⁻¹		

* The robust conditions: 1,4 kW and 6 L min⁻¹

Calibration

The calibration solutions were prepared using mono-element standard solutions: Al, Be, Cd, Co, Cr, Cu, Mn, Ni Pb, Sc, V, Zn, all 1.000 $\pm$ 0.005 g L⁻¹, all were made by Analytica Co. Ltd. (Czech Republic), and Y 10.000 $\pm$ 0.030 g L⁻¹ (made by CPI International, USA) and appropriate dilutions. We prepared multi-elements calibration standards (Table 3): all of them

contained internal standard (IS) Y and Sc (both 100 $\mu\text{g L}^{-1}$). The concentration of elements in multi-element standard is summarised in Table 3. All standards were stabilised by addition 1 mL concentrated nitric acid to 100 mL solution.

Table 3 Multi-elements calibration standards

	S ₀	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆
	[$\mu\text{g L}^{-1}$]						
Al	0	1000	400	200	160	100	80
Be	0	50	20	10	8	5	4
Cd	0	50	20	10	8	5	4
Co	0	100	40	20	16	10	8
Cr	0	200	80	40	32	20	16
Cu	0	200	80	40	32	20	16
Mn	0	100	40	20	16	10	8
Ni	0	400	160	80	64	40	32
Pb	0	800	320	160	128	80	64
V	0	200	80	40	32	20	16
Zn	0	1000	400	200	160	100	80

Artificial sample preparation

The stock solution of urine matrix was prepared according to Dawson [3]: 30.9 g $\text{NH}_4\text{H}_2\text{PO}_4$; 50.8 g NaCl; 28.6 g KCl; 3.12 g CaCO_3 ; and 4.18 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; 87 mL HCl 36.5%; 6.7 mL 98% H_2SO_4 in 1 l demineralised water (Milli Q⁺, Millipore). An organic matrix was simulated by addition of urea (181 g L^{-1} , in accordance to SRM NYC 403 125 from Nycomed). The concentrations of urine trace elements stock solution were (in mg L^{-1}): Al 10; Be 0.5; Cd 0.5; Co 1; Cr 2; Cu 2; Mn 1; Ni 4; Pb 8; V 2; Zn 10.

The artificial urine used (“urine equivalent” concentration) was prepared as follows: 100 mL of stock urine matrix and 100 mL of urine trace elements was brought in 1000 mL volumetric flask. An internal standard was added (its final concentration was 100 $\mu\text{g L}^{-1}$) and

the volumetric flask was filled up with demineralised water. Amounts of matrix component in that solution were established to be “concentration relative to urine equivalent” (CRUE). All the chemicals ($\text{NH}_4\text{H}_2\text{PO}_4$, NaCl , KCl , CaCO_3 , MgCl_2 , HCl , H_2SO_4 , HNO_3 , urea) were purity pro analyse from Lachema (Czech Republic).

Results and Discussion

Matrix Interference

Urine is a highly saline solution with variable concentrations of inorganic and organic components. Diluted salts can cause both positive and negative error in determination of analysed elements. The amount of diluted components is significantly changeable and prevents matrix matching calibration. The interference of matrix concentration level and the influence due to individual urine components (NaCl , KCl , CaCO_3 , MgCl_2 , $\text{NH}_4\text{H}_2\text{PO}_4$, HCl , H_2SO_4 and urea) and their concentration levels in ICP-AES were studied. Sets of model solutions were prepared. The first set contained always the elements estimated and a variable addition of single matrix components. The concentrations of the elements affected were the same as in the artificial urine; the concentration of influencing component CRUE was equal to 2.0. The second set contained the estimated elements and variable additions of the whole urine matrix. The concentrations of affected elements were the same as in the artificial urine; the concentration of urine matrix ranged from 0.1 to 2.0 CRUE. Direct determination of studied elements was carried out. Multi-element calibration standards and demineralised water as blank were used. Recoveries for direct estimation of trace elements in model solution (standard S_2) are summarised in Tables 4 a,b. The recoveries for affected element (its pure salt in water) are related to known content in model samples. The precision (RSD) was less than 2% for direct determination.

Table 4a Interference by model matrix. Recoveries for direct estimation [%].

Line [nm]	R [%]					
	CRUE 0.0	CRUE 0.1	CRUE 0.2	CRUE 0.5	CRUE 1.0	CRUE 2.0
Al I 308.215	100.3	99.2	98.6	93.8	89.7	88.5
Be I 234.861	99.5	95.7	91.5	89.0	86.9	82.4
Cd I 228.802	100.3	92.4	83.8	80.3	76.9	72.7
Co II 228.616	99.2	96.1	92.0	89.6	87.7	86.5
Cu I 324.754	99.5	89.0	77.7	81.8	78.7	73.9
Cr I 357.869	100.4	95.9	92.7	89.7	88.8	81.4
Mn I 403.071	99.0	94.5	91.8	88.9	84.2	79.6
Ni II 221.647	99.3	93.3	86.8	82.1	77.2	72.9
Pb I 216.999	102.0	93.1	90.0	85.1	82.4	79.3
V II 309.311	99.7	92.8	89.2	84.2	79.0	74.3
Zn I 213.856	99.3	91.1	86.0	80.1	72.9	68.6

Table 4b Interference by single matrix components (CRUE = 2,0). Recoveries for direct estimation [%].

Line [nm]	R [%]						
	Urea	HCl	H ₂ SO ₄	NaCl	KCl	CaCO ₃	MgCl ₂
Al I 308.215	103.4	102.4	101.4	79.7	88.2	97.7	95.1
Be I 234.861	102.4	100.9	100.7	84.2	88.6	89.9	91.3
Cd I 228.802	102.5	100.4	100.0	84.1	88.9	95.6	94.1
Co II 228.616	101.6	98.8	100.5	81.0	88.1	93.7	92.2
Cu I 324.754	103.4	98.7	98.6	85.1	89.0	96.1	96.4
Cr I 357.869	103.0	102.2	98.0	85.3	85.9	87.5	87.0
Mn I 403.071	101.7	99.8	100.3	83.9	87.7	95.9	94.6
Ni II 221.647	102.8	98.7	101.0	78.2	87.6	93.7	88.7
Pb I 216.999	98.8	97.2	100.2	79.0	91.5	92.7	88.6
V II 309.311	110.6	105.3	103.4	92.1	95.4	96.9	94.6
Zn I 213.856	97.8	98.8	99.2	78.7	85.5	94.8	94.4

CAIS

The CAIS technique based on simultaneous measurement of two different spectral lines of the same analyte was tested. Analyte – internal reference pairs were chosen for all the analysed elements. A large difference between the relative intensity changes of line pair is desirable. A perfect combination is atomic line – ionic line pair. However, atomic – atomic or ionic – ionic line pairs could also be used if the difference in excitation energies of working lines is large (Table 5). The line intensity and the internal reference line intensity should be affected by matrix in different ways. The results of CAIS technique in determination of trace urine elements are summarised in Table 6. The correction factor curves, e.g. dependences of the correction factor I_a^0/I_a on the line ratio I_a/I_b , are presented in Figs 1a – 1l. (I_a - analyte line intensity; I_a^0 - analyte line intensity, matrix concentration is equal to 0; I_b internal reference line intensity).

Table 5 Atomic line – ionic line pairs for the CAIS

Analyte line [nm]	Internal reference [nm]	Analyte line [nm]	Internal reference [nm]
Al I 308.215	Al II 167.081	Mn I 403.071	Mn II 257.610
Be I 234.861	Be II 313.042	Ni II 221.647	Ni I 341.476
Cd I 228.802	Cd II 226.502	Pb I 216.999	Pb II 220.353
Co II 228.616	Co I 345.350	V II 309.311	V I 318.398
Cu I 324.754	Cu II 224.700	Zn I 213.856	Zn II 206.200
Cr I 357.869	Cr II 267.716		

Internal Standardisation

The determination of chosen trace elements by the internal standardisation technique was another of the methods studied. The internal standardisation is suitable for overcoming of matrix effect when transport interferences only occur. It sometimes can be false in the case of the ionisation interferences caused by the EIE's. The commonly used Y (II 371.030 nm) and Sc (II 357.253 nm) were chosen as internal standards (IS) [7,13]. The concentration of Y and

Sc was $100 \mu\text{g L}^{-1}$, and the blank was water solution of Y or Sc ($100 \mu\text{g L}^{-1}$). The third internal standard tested was Ar. Hoenig *at al.* [14] recommended the spectral line Ar I 794.8 nm. No special preparation procedure (like that for the internal standard addition to sample) is necessary, because Ar is present as the working gas. A proper choice of suitable internal standard sufficiently decreases the transport interference, but it would fail if ionisation interference occurred. In this analysis apparently the transport interference overbalanced the ionisation interference, because both internal standards Y (II 371.030 nm) and Sc (II 357.253 nm) together provided better results than the direct determination of trace elements. Also Ar (I 794.8 nm) was tested as internal standard, but the results were fundamentally worse, due perhaps to the unsuitable spectral line choice. The precision (RSD) was about 1%. The results are summarised in Table 6.

Robust Operation Conditions

The matrix effect can be significantly minimized by applying robust operation condition, i.e. a low plasma gas flow and a high rf power level. The direct estimation of trace urine elements was carried out under the robust condition: power 1400W and plasma argon flow 6 L min^{-1} . The precision (RSD) was less than 2% for determination under the robust condition. The results are summarised also in Table 6.

Detection Limits

The statistical evaluation of regression equations for single calibration dependences was carried out by the Adstat program using the method described in textbook [25] as well as the evaluation of limits of detection. The regression models were suggested for description of the experimental data in the form $I_x = \beta_0 + \beta_1 c_x + \beta_2 c_x^2$, where C_x is concentration of the element measured (in mg L^{-1}), I_x stands for intensity of the element measured (in *counts*). For the model, the Student test was adopted to test the zero hypothesis $H_0: \beta_x = 0$ against $H_A: \beta_x \neq 0$ (for $x = 1-2$). Statistically insignificant members, for which the H_0 hypothesis had been

accepted, were left out from the general regression model; for these members it was $|t| < t_{\text{critic}}$. In case of all the tested lines and elements, only linear models are sufficient, because higher members are statistically insignificant. The limit of detection expressed as the critical value x_c [mg L⁻¹] is defined as the upper limit of confidence band of regression dependence for zero concentration in this case. The limits of detection calculated by the Adstat program (LOD's) and expressed as 3σ for pure water solution of tested elements and elements in model urine are presented in Table 7. The reference scales for trace elements in urine are presented in Table 8.

Table 6 Determination of trace elements in model urine samples.

Comparison of recoveries [%] for single correction methods. (CRUE = 2.0)

Line [nm]	R [%]					
	DE	IS-Y	IS-Sc	IS-Ar	CAIS	RC
Al I 308.215	88.5	85.2	85.1	96.6	96.2	94.2
Be I 234.861	82.4	98.7	96.3	95.7	97.0	93.5
Cd I 228.802	72.7	83.3	92.4	96.8	95.8	92.5
Co II 228.616	86.5	89.0	92.6	95.7	96.3	94.0
Cu I 324.754	81.4	94.1	94.5	90.6	95.4	96.0
Cr I 357.869	73.9	95.6	98.3	97.6	95.0	94.2
Mn I 403.071	79.6	90.7	92.3	99.6	95.2	94.1
Ni II 221.647	72.9	86.2	88.0	102.9	96.0	90.1
Pb I 216.999	79.3	83.7	95.1	98.3	97.1	89.6
V II 309.311	74.3	103.6	104.1	105.7	97.3	92.7
Zn I 213.856	68.6	82.6	91.2	103.6	95.3	90.1

DE: direct estimation, IS-Y: the internal standard Y, IS-Sc: the internal standard Sc, IS-Ar: the internal standard Ar, CAIS: common analyte internal standardisation, RC: robust operating condition

Table 7 Detection limits (direct estimation) in pure water solution and model urine sample (CRUE = 1) and reference scale of trace elements in urine [26].

Line	$3\sigma_{WS}$	LOD_{WS}	$3\sigma_{MU}$	LOD_{MU}	Reference scale	Indicated value	Metabolic anomalies
[nm]	[$\mu\text{g L}^{-1}$]						
Al I 308.215	13.077	16.440	16.92	18.50	2.30–19.5	>19.5–31.0	>31.0
Be I 234.861	0.109	0.182	0.183	0.187	0.04–0.76	>0.76–0.82	>0.82
Cd I 228.802	1.759	1.650	1.366	2.129	0.38–1.34	>1.34–2.0	>2.00
Co II 228.616	1.545	1.608	2.285	2.522	0.18–0.96	>0.96–2.0	>2.00
Cr I 357.869	1.906	3.298	1.478	3.080	0.04–1.50	>1.50–5.1	>5.10
Cu I 324.754	1.542	1.952	1.293	1.928	4.20–50.0	>50.0–75.0	>75.0
Mn I 403.071	0.190	0.791	0.245	0.796	0.12–1.90	>1.9–3.0	>3.00
Ni II 221.647	1.597	1.478	2.677	4.614	0.06–1.74	>1.74–3.90	>3.90
Pb I 216.999	8.277	11.550	10.95	11.900	12.0–27.0	>27.0–39.0	>39.0
V II 309.311	1.737	2.198	2.673	4.722	0.20–1.00	>1.00–1.44	>1.44
Zn I 213.856	0.891	3.293	0.810	1.894	266–846	>846 - 1300	>1300

LOD_{WS} : the “Adstat” limit of detection for water solution, LOD_{MU} : the “Adstat” limit of detection for model urine, $3\sigma_{WS}$: the 3σ limit of detection for water solution, $3\sigma_{MU}$: the 3σ limit of detection for model urine

Analysis of Standard Reference Material

All the discussed correction methods were evaluated with urine control material SeronomTM Trace Element Urine, batch 403125 (Nycomed Pharma), and SRM Lypocheck 69012 (Bio-Rad, Germany). The internal standards (Y, Sc - final concentration 0,1 mg L⁻¹) were added during the reconstitution of reference material. The results are summarised in Tables 8a,b.

Table 8a Analysis of of SeronomTM Trace Element Urine, lot 403125 (Nycomed Pharma)

	Declared [µg L ⁻¹]	DE [µg L ⁻¹]	IS–Y [µg L ⁻¹]	IS–Sc [µg L ⁻¹]	IS–Ar [µg L ⁻¹]	CAIS [µg L ⁻¹]	RC [µg L ⁻¹]
Al	132	113±2.27	126±1.33	121±1.02	129±1.42	135±1.69	128±1.69
Be	5	4.18±0.065	4.21±0.043	5.16±0.040	4.84±0.058	5.27±0.104	4.85±0.091
Cd	5.0	3.81±0.066	4.69±0.055	4.78±0.042	5.04±0.051	5.38±0.093	5.55±0.086
Co	10.0	8.95±0.141	9.62±0.091	9.15±0.576	9.96±0.783	10.62±0.153	10.31±0.135
Cr	20.0	18.7±0.349	19.3±0.162	19.1±0.151	19.1±0.179	21.0±0.395	20.8±0.308
Cu	28	25.3±0.387	27.1±0.021	28.1±0.171	26.7±0.216	28.4±0.480	27.3±0.412
Mn	13	13.6±0.242	12.8±0.088	12.4±0.069	12.3±0.122	14.8±2.110	12.7±0.161
Ni	40	34.9±0.569	38.9±0.276	38.2±0.218	38.5±0.306	41.2±0.667	39.0±0.542
Pb	85	80.6±1.402	82.7±0.686	83.1±0.607	78.1±1.013	87.9±1.224	83.9±1.167
V	25	25.1±0.397	24.8±0.191	25.6±0.189	23.9±0.216	24.3±0.428	26.8±0.450
Zn	450	432±8.12	428±2.78	496±4.22	432±4.23	516±9.41	418±6.77

DE: direct estimation, IS–Y: the internal standard yttrium, IS–Sc: the internal standard scandium, IS–Ar: the internal standard argon, CAIS: common analyte internal standardisation, RC: robust operating condition

Table 8b Analysis of Lypocheck 69012 (Bio-Rad)

	Declared (Accepted) [µg L ⁻¹]	DE [µg L ⁻¹]	IS–Y [µg L ⁻¹]	IS–Sc [µg L ⁻¹]	IS–Ar [µg L ⁻¹]	CAIS [µg L ⁻¹]	RC [µg L ⁻¹]
Al	115 (92-138)	90.9±1.50	106±1.06	103±0.86	113±1.12	110±0.96	110±0.99
Cd	12.8 (10.2-15.3)	12.9±0.166	13.4±0.127	13.9±0.125	12.1±0.105	12.6±0.179	13.2±0.159
Co	10.6 (8.5-12.7)	9.4±0.182	10.8±0.835	11.4±0.791	9.8±0.098	10.9±0.207	11.3±0.189
Cr	25.8 (20.7-31.0)	22.3±0.341	24.2±0.147	26.8±0.156	23.5±0.185	26.1±0.469	24.6±0.398
Cu	67 (53-80)	67.2±1.12	70.3±0.654	69.2±0.781	63.0±0.685	67.5±0.972	66.8±0.845
Mn	22.6	25.3±3.87	22.8±0.135	23.7±0.121	20.1±0.198	23.0±0.382	24.1±0.354

	(18.1-27.1)						
Ni	29.8 (23.8-35.7)	31.3±0.416	30.7±0.167	33.2±0.163	27.2±0.281	31.6±0.487	29.7±0.356
Pb	66 (53-79)	64.1±1.05	67.8±0.461	69.6±0.499	65.7±0.632	70.8±0.998	65.6±1.01
Zn	1131 (905-1358)	1275±22.3	1096±6.0	1308±9.2	1058±11.5	1016±13.5	1099±15.9

DE: direct estimation, IS–Y: the internal standard Y, IS–Sc: the internal standard Sc, IS–Ar: the internal standard Ar, CAIS: common analyte internal standardisation, RC: robust operating condition

Conclusion

The content of main matrix components in model urine (NaCl, KCl, CaCO₃, MgCl₂, NH₄H₂PO₄, HCl, H₂SO₄ and urea) is significantly changeable, hardly predicable, and prevents matrix matching. The presence of salts causes a negative error in direct determination of analysed elements. In the case of complex matrix concentration level CRUE = 2.0, the signal intensities of most elements decrease down to 30%. The sum of additions of single components exceeds the influence of complex matrix. The effect of the presence of mineral acids (HCl, HSO₄) is practically insignificant even at the highest concentration level tested (CRUE =2.0). Although the content of urea in model urine is relatively high (181 g L⁻¹, in accordance to SRM NYC 403 125 by Nycomed), the resultant effect is not strong, and the recoveries for direct estimation are approximately 100%. On the other hand, the effect of the presence of NaCl (the signal decrease down to 20%), KCl (down to 15 %) and MgCl₂ as well as CaCO₃ (down to 10 %) is significant. The precision (RSD) was less than 2 % for direct determination for all studied elements.

All the methods for matrix effect correction were only studied for complex matrix, not for the single components. In the case of all the elements except Al, internal standardisation with Y and Sc brought about a significant increase in intensity of the element measured, but

the recoveries reached up to 95% anyway. Depending on the element analysed, the internal standardisation with Ar provided a similar result that fluctuates between 90-95%. Precision of internal standardisation methods was up to 1%. In the case of CAIS method, the recoveries found were about 95% with the precision of up to 2%. The determination under the “robust condition” gave similar results as the CAIS technique.

Two ways for estimation of limits of detection were used: the limit of detection expressed as the critical value x_c (the upper limit of confidence band of regression dependence for zero concentration [26]) and “ 3σ ” for pure water solution of tested elements and elements in model urine. They were compared with reference scales for trace elements. Except the critical value for Cd in model urine and all the “LOD’s” found for V, the others are higher than the upper limits for metabolic anomalies. Considering the required “LOD’s”, the ICP-AES is suitable for analysis of trace elements in toxicologically interesting urines. The ICP-AES is cheaper and faster than the commonly used GF-AAS. The findings acquired about correction techniques are profitable in analysis of other materials where complicated matrix is expected.

All the correction methods discussed were successfully evaluated with urine control material SeronomTM Trace Element Urine, batch 403125 (Nycomed Pharma) and SRM Lypocheck 69012 (Bio-Rad, Germany).

ACKNOWLEDGEMENTS

Financial support from the Ministry of Education, Youth and Sports of the Czech Republic within project No. 253100002 and from Grant agency of Czech Republic within project No. 203/02/0023 used in this work is greatly appreciated.

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