COMPARISON OF METHODS USED FOR ELIMINATION OF MATRIX EFFECT IN ICP-AES

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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, CaCO$_3$, MgCl$_2$, NH$_4$H$_2$PO$_4$, HCl, H$_2$SO$_4$ 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 and the "CAIS" technique 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 Seronom™ Trace Element Urine, batch 403125 (Nycomed Pharma), and Lyhpochek 69012 (Bio-Rad).

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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 specialised 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 the case of trace element analysis of urine due to the 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 should 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 be used as a fast diagnostic tool in the control of ICP systems [22–24].

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 an ICP atomic emission spectrometer "Integra XL 2" from GBC, Australia. The emission lines used are listed in Table I; the measuring parameters are listed in Table II.

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 ± 0.005 g l^{-1}, all were made by Analytica Co. Ltd. (Czech Republic), and Y 10.000 ± 0.030 g l^{-1} (made by CPI International, USA) and appropriate dilutions. We prepared multi-elements calibration standards (Table III): all of them contained internal standard (IS) Y and Sc (both 100 µg l^{-1}). The concentration of elements in multi-element standard is

Table I 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 II	727.294	1	dynamic
Mn I	403.071	1	± 0.0270	Sc II	357.253	1	± 0.0320

Table II 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
Auxilliary gas flow	0.50 l min^{-1}		
Nebulizer gas flow	0.60 l min^{-1}		

Table III Multi-elements calibration standards — concentration in $\mu g\ l^{-1}$

	S_0	S_1	S_2	S_3	S_4	S_5	S_6
Al, Zn	0	1000	400	200	160	100	80
Be, Cd	0	50	20	10	80	5	4
Co, Mn	0	100	40	20	16	10	8
Cr, Cu, V	0	200	80	40	32	20	16
Ni	0	400	160	80	64	40	32
Pb	0	800	320	160	128	80	64

summarised in Table III. All standards were stabilised by addition 1 ml concentrated nitric acid to 100 ml solution.

Artificial Sample Preparation

The stock solution of urine matrix was prepared according to Dawson [3]: 30.9 g $NH_4H_2PO_4$; 50.8 g NaCl; 28.6 g KCl; 3.12 g $CaCO_3$; and 4.18 g $MgCl_2 \cdot 6H_2O$; 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 µg 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 ($NH_4H_2PO_4$, 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

The interference of matrix concentration level and the influence due to individual urine components (NaCl, KCl, $CaCO_3$, $MgCl_2$, $NH_4H_2PO_4$, 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 IV and V.

CAIS

The CAIS technique based on simultaneous measurement of two different spectral lines of the same analyte was tested. Analyte — internal reference pairs were cho-

Table IV 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 V Interference by single matrix components (CRUE = 2.0). Recoveries for direct estimation [%]

Line, nm	R, %						
	Urea	HCl	H_2SO_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

Table VI 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 227.700	Zn I 213.856	Zn II 206.220
Cr I 357.869	Cr II 267.716		

Table VII Determination of trace elements in model urine samples. Comparison of recoveries [%] for single correction methods. (CRUE = 2.0)

Element	R, %				
	DE	IS-Y	IS-Sc	IS-Ar	CAIS
Al	88.5	85.2	85.1	96.6	96.2
Be	82.4	98.7	96.3	95.7	97.0
Cd	72.7	83.3	92.4	96.8	95.8
Co	86.5	89.0	92.6	95.7	96.3
Cu	81.4	94.1	94.5	90.6	95.4
Cr	73.9	95.6	98.3	97.6	95.0
Mn	79.6	90.7	92.3	99.6	95.2
Ni	72.9	86.2	88.0	102.9	96.0
Pb	79.3	83.7	95.1	98.3	97.1
V	74.3	103.6	104.1	105.7	97.3
Zn	68.6	82.6	91.2	103.6	95.3

DE – direct estimation; IS-Y – the international standard Y; IS-Sc –the internal standard Sc; IS-Ar – the internal standard Ar; CAIS – common analyte internal standardisation

sen 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 VI). 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 VII. 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 Fig. 1. (I_a – analyte line intensity; I_a^0 – analyte line intensity, matrix concentration is equal to 0; I_b – internal reference line intensity).

Internal Standardisation

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 [7,13]. The concentration of Y and Sc was 100 μg l^{-1}, and the blank was water solution of Y or Sc (100 μg l^{-1}). The third internal standard tested was Ar. Hoenig et al. [14] recommended the spectral line Ar I 794.8 nm. 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 VII.

Detection Limits

The statistical evaluation of regression equations for single calibration dependences was carried out by the Adstat program using the method described [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 $|t| < t_{critic}$. In the 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 VIII. The reference scales for trace elements in urine are presented in Tables IX and X.
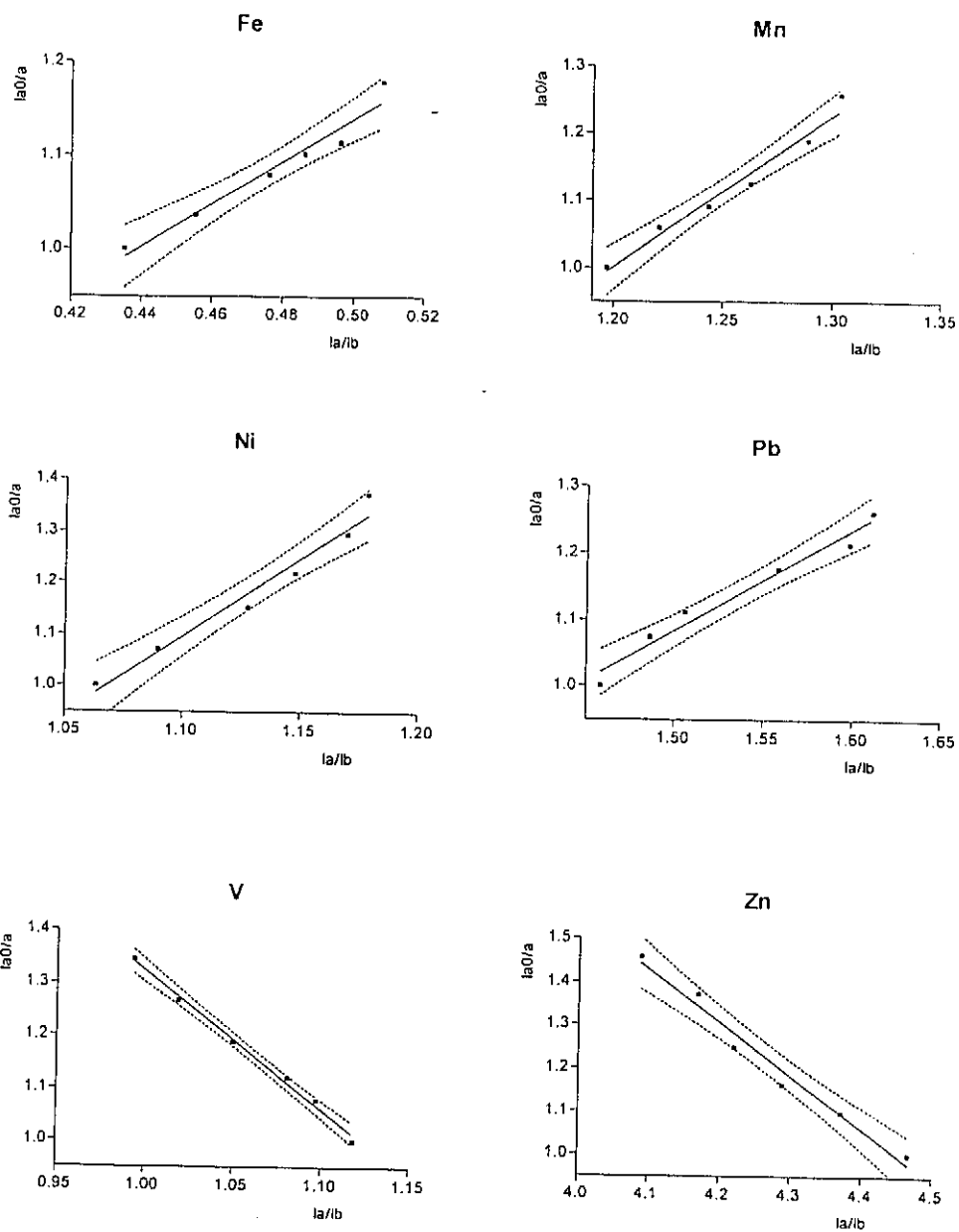
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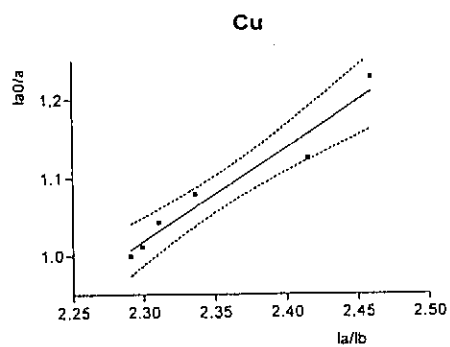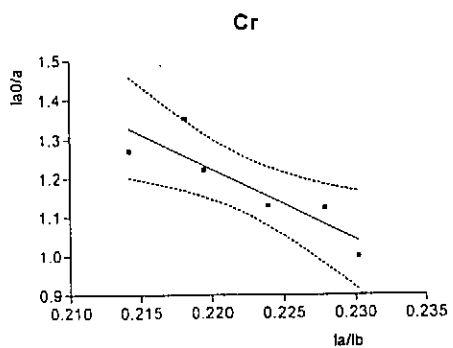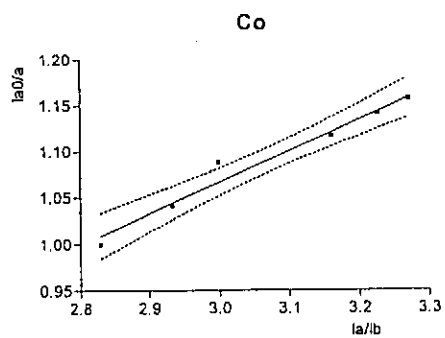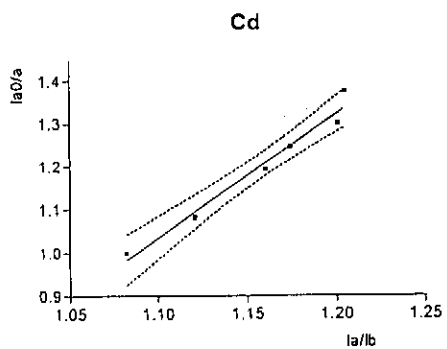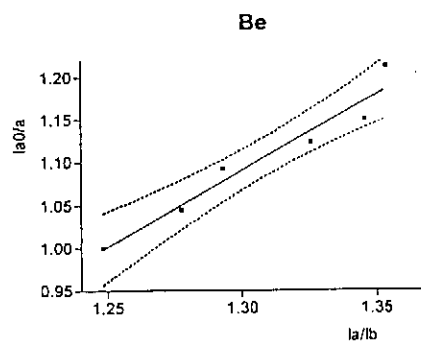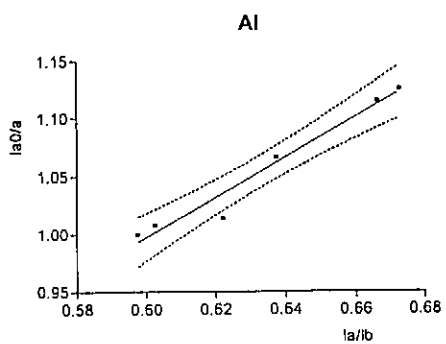
Fig. 1 The CAIS technique — dependence of the correction factor I_a^0/I_a on the line ratio I_a/I_b (I_a – analyte line intensity; I_a^0 – analyte line intensity, matrix concentration is equal to 0; I_b – internal reference line intensity)

Table VIII Detection limits (direct estimation) in pure water solution and model urine sample (CRUE = 1) and standard reference scale of trace elements in urine

Line, nm	$3\sigma_{WS}$	LOD_{WS}	$3\sigma_{MU}$	LOD_{MU}	Reference scale	Indicated value	Metabolic anomalies
					µg l⁻¹		
Al I 308.215	13.1	16.4	17.0	18.5	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	1.74	1.65	1.37	2.13	0.38 – 1.34	>1.34 – 2.0	>2.0
Co II 228.616	1.55	1.61	2.29	2.52	0.18 – 0.96	>0.96 – 2.0	>2.0
Cu I 324.754	1.91	3.30	1.488	3.08	0.04 – 1.50	>1.50 – 5.1	>5.10
Cr I 357.869	1.54	1.95	1.298	1.93	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	1.60	1.48	2.68	4.61	0.06 – 1.74	>1.74 – 3.9	>3.90
Pb I 216.999	8.28	11.6	11.0	11.9	12.0 – 27.0	>27.0 – 39.0	>39.0
V II 309.311	1.74	2.20	2.67	4.72	0.20 – 1.00	>1.00 – 1.44	>1.44
Zn I 213.856	0.891	3.30	0.810	1.89	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 Seronom™ Trace Element Urine, batch 403125 (Nycomed Pharma), and SRM Lyphochek 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 IX and X.

Conclusion

The content of main matrix components in model urine 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,

Table IX Analysis of Seromon™ Trace Element Urine, (concentration in μg l^{-1})

	Declared	DE	IS-Y	IS-Sc	IS-Ar	CAIS
Al	132	113 ± 2.27	126 ± 1.33	121 ± 1.02	129 ± 1.42	135 ± 1.69
Be	5	4.18 ± 0.065	4.21 ± 0.043	5.16 ± 0.040	4.84 ± 0.058	5.27 ± 0.104
Cd	5.0	3.81 ± 0.066	4.69 ± 0.055	4.78 ± 0.042	5.04 ± 0.051	5.38 ± 0.093
Co	10.0	8.95 ± 0.141	9.62 ± 0.091	9.15 ± 0.576	9.96 ± 0.783	10.62 ± 0.153
Cr	20.0	18.7 ± 0.349	19.3 ± 0.162	19.1 ± 0.151	19.1 ± 0.179	21.0 ± 0.395
Cu	28	25.3 ± 0.384	27.1 ± 0.021	27.1 ± 0.171	26.7 ± 0.216	28.4 ± 0.480
Mn	13	13.6 ± 0.242	12.8 ± 0.088	12.4 ± 0.069	12.3 ± 0.122	14.8 ± 2.11
Ni	40	34.9 ± 0.569	38.9 ± 0.276	38.2 ± 0.218	38.5 ± 0.306	41.2 ± 0.667
Pb	85	80.6 ± 1.402	82.7 ± 0.686	83.1 ± 0.607	78.1 ± 1.013	87.9 ± 1.224
V	25	25.1 ± 0.397	24.8 ± 0.191	25.6 ± 0.189	23.9 ± 0.216	24.3 ± 0.428
Zn	450	432 ± 8.12	428 ± 2.78	496 ± 4.22	432 ± 4.23	516 ± 9.41

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;

Table X Analysis of Lyphochek 69012 (concentration in μg l^{-1})

	Declared (Accepted)	DE	IS-Y	IS-Sc	IS-Ar	CAIS
Al	115 (92 – 138)	90.9 ± 1.50	106 ± 1.06	103 ± 0.86	113 ± 1.12	110 ± 0.96
Cd	12.8 (10.2 – 15.3)	12.9 ± 1.66	13.4 ± 0.127	13.9 ± 0.125	12.1 ± 0.105	12.6 ± 0.179
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
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
Cu	67 (53 – 80)	67.2 ± 1.12	70.3 ± 0.654	69.2 ± 0.781	63.0 ± 0.685	67.5 ± 0.972
Mn	22.6 (18.1 – 27.1)	25.3 ± 3.87	22.8 ± 0.135	23.7 ± 0.121	20.1 ± 0.198	23.0 ± 0.382
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
Pb	66 (53 – 79)	64.1 ± 1.05	67.8 ± 0.461	69.6 ± 0.499	65.7 ± 0.632	70.8 ± 0.998
Zn	1131 (905 – 1358)	1275 ± 22.3	1096 ± 6.0	1308 ± 9.2	1058 ± 11.5	1016 ± 13.5

The meaning of symbols is the same as in Table IX

H_2SO_4) 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 $MgCl_2$ as well as $CaCO_3$ (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 9 % with the precision of up to 2 %.

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 [25]) 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 Seronom™ Trace Element Urine, batch 403125 (Nycomed Pharma) and SRM Lyphochek 69012 (Bio-Rad, Germany).

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