

ET-AAS determination of aluminium in dialysis concentrates after continuous flow solvent extraction

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Abstract

Conditions of a continuous flow extraction (CFE) of aluminium acetylacetonate in acetylacetone and aluminium 8-hydroxyquinolate into methylisobutylketone (lengths of reaction and extraction coils, flow rates of aqueous and organic phases and their flow rate ratio, pH of aqueous phase, lengths of coils for transport of aqueous and organic phases and effect of salts) were studied. The analytical signal of the aluminium chelates present in the organic phase was measured at 309.3 nm using atomic absorption spectrometry with electrothermal atomization (ET-AAS) at the flow rate ratio $F_{\text{aq}}/F_{\text{org}} = 3$ for aqueous and organic phases. The five points calibration curves were linear (R^2 0.9973 and 0.9987) up to $21 \mu\text{g l}^{-1}$ Al with the limits of detection of $0.3 \mu\text{g l}^{-1}$ and the recovery $100 \pm 2\%$ and precision of 3% at 2–10-fold dilution of the dialysis concentrates. The acetylacetonate method was applied to the determination of aluminium in real dialysis concentrates. Aluminium in concentrations $5\text{--}6 \mu\text{g l}^{-1}$ (R.S.D.s 5–10% in real samples) were found and the results were in the very good agreement with those obtained by an ET-AAS using preconcentration of Al(III) on a Spheron-Salicyl chelating sorbent (absolute and relative differences were under $0.4 \mu\text{g l}^{-1}$ and 8.2%, respectively). © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

It is hard to believe that the third widely spread element in the earth crust has toxic effects to mammals, aquatic organisms, plants, etc. even at very low concentrations. It was also observed a conjunction of aluminium contamination of foods and drinking water with human diseases such as arteriosclerosis and Alzheimer's disease [1–4]. The neurotoxicity of aluminium is directly linked to its bioavailability. The ingestion of aluminium from both the food and drinking water is the most common form of human exposure.

The serious toxic effect of aluminium was observed also on patients with renal failure subjected to dialysis, such as anemia, encephalopathy and dialysis dementia [1–4]. It was confirmed that decrease of aluminium content under critical level has a preventive effect. The dialysis fluids are prepared from dialysis

concentrates that are mixed with pure water. If aluminium is present as a contaminant in these fluids, it is able to diffuse through the dialysis membranes and penetrate into the blood stream of the patient. The contamination levels in these cases depend strongly on the quality of the water and the dialysis concentrates used in the dialysis fluid preparation. The Official Pharmacopeias [5] require an accurate control of the trace levels of aluminium in commercial dialysis solutions, which must be lower than $10 \mu\text{g l}^{-1}$.

Hence, a simple and sensitive method is of primary importance for the effective monitoring of aluminium present as contaminant in dialysis concentrates [6]. The complex matrix with high levels of sodium ($2\text{--}5 \text{ mol l}^{-1}$), calcium ($0.03\text{--}0.05 \text{ mol l}^{-1}$), magnesium ($0.01\text{--}0.02 \text{ mol l}^{-1}$) and potassium ($0\text{--}0.07 \text{ mol l}^{-1}$) as chlorides, sodium acetate or bicarbonate, sodium lactate and glucose, respectively [7], makes dialysis concentrates difficult to analyse.

Lack of sensitivity and difficulty in sample handling due to contamination are the major problems that usually impair the determination of aluminium at ultra trace levels. Suitable

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techniques for monitoring and determination of aluminium at trace levels are therefore necessary [8]. Inductively coupled plasma atomic emission spectrometric (ICP-AES), flame atomic absorption spectrometric (FAAS) and spectrophotometric methods with higher limit of detection need preconcentration of the analyte [8–11]. Fluorimetric methods are very sensitive, but they usually lack selectivity [12,13]. The fluorimetric extractive procedure is suitable for the toxicological control of aluminium traces in dialysis solutions [14–18].

An adsorptive stripping voltammetric (AdSV) determination of aluminium may overcome the problems caused by the high salt content of dialysis concentrates, but it needs very careful elimination of organic matter. Solochrome violet RS [19] and 1,2-dihydroxyanthra-quinone-3-sulfonic acid (DASA) were used as complexing agents for the determination of aluminium in dialysis fluids with detection limit $0.8 \mu\text{g l}^{-1}$ [6].

Sensitive methods such as inductively coupled plasma mass spectrometry (ICP-MS) that has recently been proposed for the determination of aluminium in dialysis samples [20] has acceptable detection limits and does not need preconcentration. Its susceptibility to matrix effects means that standard additions must be used for each sample. Separation step is also suitable [8,21]. High cost of basic ICP-MS instrumentation and relatively high operation costs are the main drawbacks of its routine applications.

Atomic absorption spectrometry with electrothermal atomization (ET-AAS) suffers from serious matrix interferences and contamination problems. Analysis of dialysis concentrates cannot be directly carried out by ET-AAS due to the high salt content. About 400 g l^{-1} of essentially chlorides causes matrix interferences and additionally, insufficient precision since the aluminium content in these fluids is normally close to the limits of detection [10]. To reduce matrix effects in ET-AAS determinations, dialysis concentrates have been analysed after up to 35-fold dilution with water [20]. The usual practice of diluting the sample aggravates the problem and leads to poor results. Addition of nitric acid [22] or orthophosphoric acid [23] as a matrix modifier was also used to minimise matrix effects. The results obtained were not reliable since the salt content in the solutions was still high [7].

Adsorption of traces of Al on sorbents and solvent extractions of its chelates are used as common separation and/or preconcentration techniques. Chromotrope 2B (1,8 dihydroxy-2-(*p*-nitrophenylazo)-naphthalene-3,6-disulphonic acid) immobilized on AG 1-X8 ion exchange resin [8,17], solid phase 8-hydroxyquinoline derivative Kelex 100 immobilised on Amberlite XAD-7 [25], Chelex-100 [7,20] chelating ion-exchange resin, desferrioxamine immobilized on porous glass [24] microcolumns and preconcentration of aluminium-Chromazurol S chelate on a polyethylene powder [9,10] were applied.

The aim of this work, therefore, was to develop and establish a simple and cost effective method (compare to ICP-MS) for Al determination in dialysis concentrates using continuous flow solvent extraction (CFE) and quantification by ET-AAS. A homemade apparatus for CFE was constructed. The influence of lengths of reaction and extraction coils, lengths of restric-

tion coils for transport of aqueous and organic phases from a membrane phase separator, flow rates of both liquids, volume and way of injection of chelating reagents, pH of aqueous phase and aqueous to organic phase flow rate ratios on separation and extraction efficiencies were evaluated.

2. Materials and methods

2.1. Instrumentation

A Perkin-Elmer atomic absorption spectrometer (model 3030) equipped with a HGA-400 graphite tube atomizer and an AS-1 autosampler was used for the ET-AAS measurements. Injection volume was $20 \mu\text{l}$. Aluminium absorption was measured at 309.3 nm . The spectral bandwidth was set at 0.7 nm . A hollow cathode lamp Intensitron at 21 mA was used as a radiation source and a deuterium lamp was used for background correction. A peristaltic pump (FIA 20 Analyzer, Villa-Labeco, S.N. Ves, Slovakia) was applied for delivery of solutions in CFE.

The electro-graphite tube without pyrolytic coating using a mini-flow mode 50 ml min^{-1} Ar was used during an atomization step. Absorbance and integrated absorbance were measured. The HGA-400 parameters were set as follows: $150^\circ\text{C}/15 \text{ s}/25^\circ\text{C}/1200^\circ\text{C}/15 \text{ s}/15^\circ\text{C}/2400^\circ\text{C}/0 \text{ s}/4 \text{ s}/2550^\circ\text{C}/1 \text{ s}/2 \text{ s}$ for all ET-AAS measurements.

Teflon cups used for the autosampler AS-1 were cleaned with 15% HCl for 24 h and then rinsed with bi-distilled water prior to analysis. The Teflon capillary of autosampler AS-1 was washed with bi-distilled water; when sampling of MIBK extracts with 20% ethanol. All operations were conducted under controlled atmosphere in an aseptic clean-box Fatran LF (Chirana, Brno, Czech Republic).

2.2. Reagents and solutions

All chemicals were of analytical reagent grade. Water was freshly quartz distilled and deionized (Milli-Q System, Millipore, Bedford, USA). All glassware and Teflon material were soaked in nitric acid (1:1) for 1 day and rinsed with deionized water before use. Plastic material was used to avoid contamination. Calibrated polyethylene flasks were immersed for 24 h in a 10% HNO_3 solution and then thoroughly rinsed with Milli-Q water before use. No contamination problems were found.

Aluminium stock solution (1000 mg l^{-1}) was prepared by dissolving 1.0136 g aluminium metal (purity $>99.99\%$) in 18.8 ml of HCl (37%, Sigma–Aldrich, Schnelldorf, Germany) and diluted up to 1000 ml with deionized water. Working aluminium standards were prepared daily by diluting the stock solution in 10 mmol l^{-1} hydrochloric acid.

8-Hydroxyquinoline (8-HQ) of analytical purity grade (Pliva-Lachema Brno, Czech Republic) was dissolved in methylisobutylketone (MIBK) to give 1% concentration. The 2 mmol l^{-1} aqueous solution of 8-HQ was prepared by dissolving of 8-HQ in 20 mmol l^{-1} HCl. Acetylacetone (AA) of p.a. purity (all Penta, Chrudim, Czech Republic) was used as a chelating and an extraction reagent.

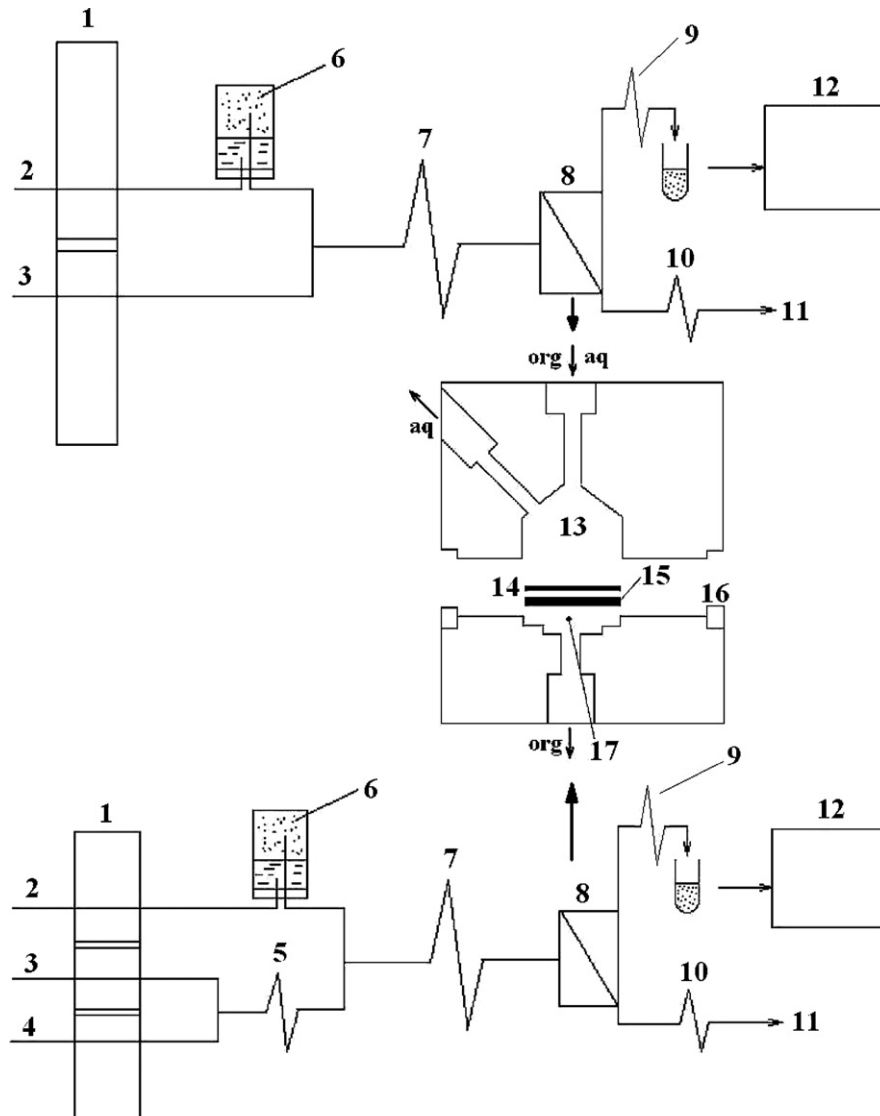


Fig. 1. Flow extraction systems with a chelating reagent in an organic solvent (top) and in an aqueous solution (bottom). (1) Pump, (2) water, (3) sample, (4) reagent, (5) reaction coil, (6) organic phase, (7) extraction coil (l_{ext}), (8) phase separator (detail in the middle), (9) coil for organic phase (l_{org}), (10) restriction coil (l_{aq}), (11) waste (aq), (12) ET-AAS, (13) separation chamber, (14) membrane, (15) metallic membrane support, (16) sealing ring, (17) chamber with separated organic phase.

Buffer solutions of pH 3–6 and 6–9 were prepared by mixing appropriate amounts of 10 mmol l^{-1} hydrochloric acid with 10 mmol l^{-1} sodium formiate (Sigma–Aldrich, Schnellendorf, Germany) and 10 mmol l^{-1} TRIS (Pliva-Lachema, Brno, Czech Republic), respectively. A mixed solution of salts ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , sodium acetate in concentrations 6, 10.1, 220 and 160 g l^{-1} , respectively) was prepared by dissolving appropriate amounts of the salts (all Pliva-Lachema, Brno, Czech Republic) in deionized water.

2.3. Procedures

A CFE manifold designed and optimized for Al extraction with a chelating reagent (AA) in an organic solvent (Fig. 1, top) and with a chelating reagent (8-HQ) in an aqueous solution (Fig. 1, bottom), was used. It consisted of Teflon capillaries (inner diameter 0.6 mm), a Teflon segmentor and a separator of

phases. Water solutions were delivered with a peristaltic pump (FIA 20 Analyzer, Villa-Labeco, S.N. Ves, Slovakia) and an organic solvent by using a glass discharge bottle with a Teflon cap. The phase separator (Fig. 1, middle) consisted of two Teflon parts bearing Sartorius Teflon membrane (Sartorius, Goettingen, Germany, Cat. No. 118 03 $1.20 \mu\text{m}$) supported with a metallic membrane with Teflon surface.

2.3.1. Procedure with a chelating reagent in an aqueous solution

The aqueous solutions of a sample and a chelating reagent (8-HQ) were merged in a Y-type mixer at the equal flow rates 0.6 ml min^{-1} using two equal capillaries (see Fig. 1, bottom). The merged flow was homogenized to form an Al-chelate in a reaction coil ($l_{\text{react}} = 30 \text{ cm}$). The aqueous solution of the aluminium-hydroxyquinolate was transported at the flow rate 1.2 ml min^{-1} into the Teflon cylindrical segmentor.

A segmented flow was created in the segmentor mixing the aqueous stream with an organic solvent at flow rates 0.3 ml min^{-1} . Extraction of the aluminium chelates from the aqueous solution into an organic solvent (aluminium 8-hydroxyquinolate into methylisobutylketone) proceeded in the extraction coil ($l_{\text{ext}} = 400 \text{ cm}$) inter-connecting the segmentor and the phase separator. Separation of the organic phase from the aqueous solution was realized in the membrane phase separator. The separated organic phase containing the Al-chelate was collected in vessels of the automatic AS-1 autosampler using restriction coil ($l_{\text{org}} = 4.5 \text{ cm}$). The length of restriction coil l_{aq} affecting pressure ratios on the membrane was 1.5 cm . Finally, the aluminium concentration was measured by ET-AAS.

2.3.2. Procedure for chelating reagents (AA or 8-HQ) in organic solvents

The aqueous solutions of a sample were introduced directly into the Teflon cylindrical segmentor (see Fig. 1, top) at the flow rate 1.2 ml min^{-1} together with 1% 8-HQ in MIBK or with acetylacetone (0.4 ml min^{-1}). Extraction of the AA or 8-HQ chelates proceeded in the extraction coil ($l_{\text{ext}} = 400 \text{ cm}$). Separation of the organic phase proceeded as described above.

3. Results and discussion

3.1. Optimization of parameters for continuous flow extraction systems

3.1.1. Effects on separation efficiency

The separation efficiency (expressed as a ratio of the separated organic phase to the total amount of the organic phase; in %) was influenced mainly by the length of the restriction capillaries for outlet of the organic phase (l_{org}) and aqueous phase (l_{aq}) from the phase separator. The flow rate ratio of both phases leaving the phase separator affects pressure ratios on the membrane and can be simply regulated changing the parameters of the restriction coils (i.d., length). Volumes of the separated organic phase and the unseparated organic phase transported together with the aqueous phase to a waste were measured in 5-min periods using a graduated cylinder.

Improper function of the discharge bottle (reservoir of the organic solvent—AA or MIBK, respectively) was observed at the flow rate ratio $F_{\text{aq}}/F_{\text{org}} > 7$ for both solvents. The flow of the organic phase was restricted in the system in the case. The penetration of the aqueous solution from the discharge bottle into the outlet capillary reduced (or restricted) the flow of the organic solvent from the bottle to the phase segmentor.

Penetration of droplets of the aqueous phase across the membrane phase separator was observed when the length of the restriction capillary for the aqueous phase was $l_{\text{aq}} > 2 \text{ cm}$ (too high overpressure on the membrane) and/or at the flow rate ratio $F_{\text{aq}}/F_{\text{org}} \geq 4$. Therefore, the length of the restriction coil was reduced to $l_{\text{aq}} = 1.5 \text{ cm}$ to eliminate the problem. Maximum separation efficiency (80%) of the two phases was constant for $l_{\text{org}} = 4\text{--}6 \text{ cm}$ at $l_{\text{aq}} = 1.5 \text{ cm}$ and at the total length of the extraction coil $l_{\text{ext}} = 400 \text{ cm}$.

Extraction coil length ($l_{\text{ext}} = 400 \text{ cm}$), restriction coil length ($l_{\text{aq}} = 1.5 \text{ cm}$), the length of the restriction capillary for outlet of the organic phase $l_{\text{org}} = 4.5 \text{ cm}$ and the maximal applicable flow rate ratio of the phases $F_{\text{aq}}/F_{\text{org}} = 3$, were selected to be optimal conditions for all extraction systems and were used for all further experiments.

3.1.2. Factors influencing extraction efficiency

The extraction efficiency (expressed as a ratio of the amount of aluminium extracted in organic phase to the total amount of aluminium in the aqueous phase; in %) was dependent especially on the length of the extraction coil and on the flow rate ratio $F_{\text{aq}}/F_{\text{org}}$. The efficiency increased rapidly to $l_{\text{ex}} = 250 \text{ cm}$, then slowly increased up to 300 cm and was practically constant over 300 cm ; therefore, $l_{\text{ex}} = 400 \text{ cm}$ was used. The dependence of the analytical signal of the organic phase on the flow rate of the aqueous phase (F_{aq}) was measured for three different systems (i) with 1% 8-HQ in MIBK, (ii) with 2 mmol l^{-1} aqueous solution of 8-HQ using MIBK as the extraction agent and (iii) with acetylacetone as an extraction and chelating agent. The flow rate of the aqueous phase was varied in the interval $0.3\text{--}1.2 \text{ ml min}^{-1}$. The highest value of the analytical signal of the organic phase, and of course the sensitivity of the method, was found for the system with acetylacetone (see Fig. 2). The following extraction efficiencies 100, 99, 99, 98% were found for extraction system with acetylacetone and 97.0, 95.2, 91.8, 89.1% for extraction system with 8-HQ in MIBK at $F_{\text{aq}}/F_{\text{org}} = 1, 2, 3$ and 4, respectively. The extraction efficiency for the system with 8-HQ in aqueous solution and with extraction into MIBK was approximately 5% lower comparing with the extraction systems with 8-HQ in MIBK. For that reason, extraction with 8-HQ in MIBK and that with acetylacetone were preferred.

3.2. Optimization of ET-AAS determination

The repeatability of the dosing of Al-acetylacetonate in acetylacetone and Al^{3+} aqueous solution was acceptable ($\text{R.S.D.s} \leq 1.1\%$, $n = 10$) when the routine procedure for sampling of the solutions into the graphite tube with Teflon capillary

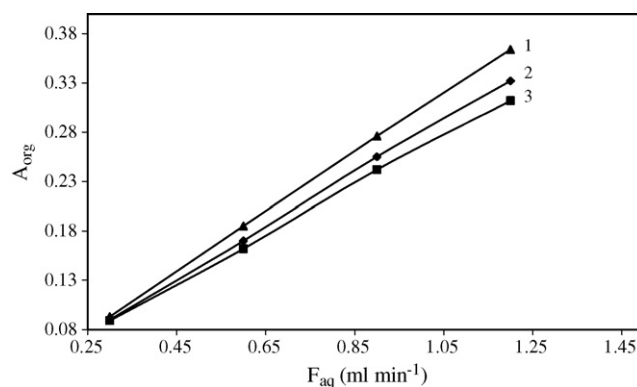


Fig. 2. The dependence of the absorbance of the organic phase (A_{org}) on the flow rate of the aqueous solution (F_{aq}) for system with acetylacetone (▲), 8-HQ solution in MIBK (◆) and with aqueous solution of 8-HQ with extraction into MIBK (■).

of the autosampler AS-1 and subsequent washing of capillary with redistilled water was applied. The corresponding R.S.D.s $\leq 2.5\%$ ($n=10$) and the signal by 15% lower were obtained for the solution of the Al-8-HQ chelate in MIBK. This is probably due to the incomplete dosing of the organic extract into the graphite tube. Careful washing of the Teflon capillary with the 20% ethanol seriously improved the repeatability of the dosing of the MIBK extract (R.S.D.s $\leq 1.6\%$, $n=10$) and increased the relative signal up to 100%.

3.3. Effect of pH of the aqueous solution

The relationships between the analytical signal of the organic phase after the extraction and the pH values aqueous solutions for the systems of extraction with 8-HQ in MIBK and with acetylacetonate are presented in Fig. 3. The pH was adjusted with 10 mmol l^{-1} TRIS and 10 mmol l^{-1} HCl for 8-HQ and with 10 mmol l^{-1} HCOONa and 10 mmol l^{-1} HCl for acetylacetonate. The optimal pH values (4.0 and 8.0) were found for extraction with acetylacetonate and 8-HQ, respectively.

3.4. Analytical performance

The extracts of aluminium chelate with 8-HQ and acetylacetonate were stable more than 10 days since the absorbance signal was constant in the time of measurement in 10 days. Thus the extracts do not need be measured in the day of the extraction.

The recovery of aluminium was verified using the solutions of aluminium with the concentration of salts in the solutions corresponding to the concentration of the substances in the dialysis concentrates (see Section 2.2) or in the presence of individual electrolytes (see Table 1) using the CFE system with acetylacetonate and 8-HQ in MIBK. The measurement confirmed $100 \pm 2\%$ recovery and accuracy $100 \pm 3\%$ at 2–10-fold dilution of the dialysis concentrates. Five points calibration curves for $F_{\text{aq}}/F_{\text{org}}=3$ were linear up to $21 \mu\text{g l}^{-1}$. Correlation coefficients R^2 were 0.9987 for 8-HQ and 0.9973 for AA, respectively. Limits of detection (LODs, $S/N=3$ criterion) of $0.3 \mu\text{g l}^{-1}$ were achieved for extraction of Al, both with 8-HQ in MIBK and with acetylacetonate. The R.S.D.s for two-fold diluted concentrate with addition of 20.3 ng ml^{-1} Al was 2.05

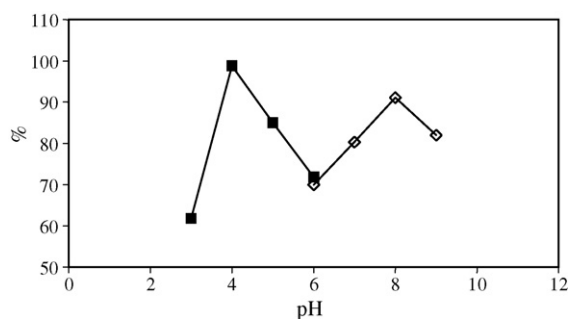


Fig. 3. The effect of pH on the extraction efficiency (in %) of the CFE system for extraction system with acetylacetonate (■) and with 8-HQ in MIBK (◇), $c_{\text{Al}}=20.3 \text{ ng ml}^{-1}$.

Table 1
Recovery of aluminium from salts solutions ($c_{\text{Al}}=20.3 \text{ ng ml}^{-1}$)

Salt	c (g l^{-1})	Recovery of Al	
		8-HQ in MIBK	Acetylacetonate
MgCl ₂ ·6H ₂ O	6	100 ± 2	100 ± 2
CaCl ₂ ·2H ₂ O	3.4	100 ± 2	–
CaCl ₂ ·2H ₂ O	6.7	94 ± 2	–
CaCl ₂ ·2H ₂ O	10.1	84 ± 2	100 ± 2
NaCl	100	100 ± 2	–
NaCl	150	99 ± 2	–
NaCl	200	79 ± 2	–
NaCl	220	78 ± 2	100 ± 2
Na-acetate	160	100 ± 2	100 ± 2
Mixture of salts	Conc. ^a	67 ± 3	83 ± 2
Mixture of salts	2× Diluted	100 ± 2	100 ± 2
Mixture of salts	5× Diluted	100 ± 2	100 ± 2
Mixture of salts	10× Diluted	100 ± 2	100 ± 2

^a 6 g l^{-1} MgCl₂·6H₂O, 6.6 g l^{-1} CaCl₂·2H₂O, 220 g l^{-1} NaCl, 160 g l^{-1} CH₃COONa.

and 1.8% ($n=5$) for 8-HQ and acetylacetonate extraction, respectively.

3.5. Analyses of dialysis concentrates

The proposed CFE/ET-AAS method with acetylacetonate was applied for the determination of aluminium in real dialysis concentrates (Table 2) obtained from the Department of Dialysis and Nephrology of the Faculty Hospital, Brno-Bohunice. The pH values of the diluted concentrates were adjusted by 0.1 mol l^{-1} sodium formiate to pH 4 and the extraction with acetylacetonate was performed. The results were in the very good experimental agreement with those obtained by ET-AAS using sorbent preconcentration of Al(III) on Spheron-Salicyl 1000 (Pliva-Lachema, Brno, Czech Republic, 40–63 μm particle size) sorbent at pH 4 (formiate buffer medium) and elution with 2 mol l^{-1} HCl (see Table 2). Absolute and relative differences were under $0.4 \mu\text{g l}^{-1}$ and between 3.3 and 8.2%, respectively. The repeatability (R.S.D.s = 4.8–9.7%) was satisfactory. The concentrations of aluminium in all the dialysis concentrates were under the declared (maximal acceptable) levels ($<10 \mu\text{g l}^{-1}$) according the official Pharmacopeias [5].

Table 2
Analysis of the real dialysis concentrates

Sample ^a	CFE/ET-AAS ^b			
	c_{Al} ($\mu\text{g l}^{-1}$)	R.S.D. (%) ^c	c_{Al} ($\mu\text{g l}^{-1}$)	R.S.D. (%) ^c
F-50	6.1	9.7	6.3	10.2
F-08	4.9	5.2	4.5	7.6
F-17	4.9	4.8	5.1	6.1

^a Salt concentrations in all dialysis concentrates in g l^{-1} : 214.77 NaCl, 3.56 MgCl₂·6H₂O, 6.31 CH₃COONa (99%); with extra addition of 5.22 g KCl, 5.15 g CaCl₂·2H₂O (F-50), 7.83 g KCl, 9.01 g CaCl₂·2H₂O for F-08; with extra addition of 5.22 g KCl, 6.43 g CaCl₂·2H₂O, 38.5 g glucose monohydrate for F-17.

^b ET-AAS using preconcentration Al(III) on Spheron-Salicyl chelating sorbent at pH 4 and elution with 2 mol l^{-1} HCl.

^c $n=7$.

4. Conclusions

The extraction of Al-acetylacetonate chelate followed by the ET-AAS quantification is suitable for the control of the traces of Al in dialysis concentrates. The method is much faster compared to the classical batch analyses mainly due to the application of fully automated CFE extraction procedure (shorter extraction times, faster phase separation) and highly reproducible and sensitive. The LODs were similar ($0.3 \mu\text{g l}^{-1}$) to that obtained with fluorimetric extractive procedure with mordant dyestuff [15], but better than for fluorimetric extractive procedure with 8-HQ ($0.7 \mu\text{g l}^{-1}$) [16], flow injection spectrophotometric determination based on the reaction of Al with eriochrome cyanine R associated with cetyltrimethylammonium bromide ($3.24 \mu\text{g l}^{-1}$) [26], ET-AAS after preconcentration on microcolumns filled with Chelex 100 resin ($0.5 \mu\text{g l}^{-1}$) [7] and adsorptive stripping voltammetry ($0.8 \mu\text{g l}^{-1}$) [6]. On the other hand, they were worse than for ICP-MS after preconcentration on a microcolumn packed with Chromotrope 2B immobilized on AG1-X8 resin ($0.1 \mu\text{g l}^{-1}$) [8] and extraction spectrophotometric determination of aluminium with 3,5-ditertbutylsalicylfluorone and ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate ($0.06 \mu\text{g l}^{-1}$) [18]. Our method is simpler and less expensive than the ICP method. It does not require “clean laboratory” and costly instrument and thus it is very suitable for most routine clinical laboratories.

Aluminium in concentrations $5\text{--}6 \mu\text{g l}^{-1}$ (R.S.D.s 5–10%) in the real dialysis concentrates were found that was under the maximal acceptable levels ($<10 \mu\text{g l}^{-1}$) according to the official legislative recommendations. Control of the Al in dialysis concentrates is one of the most important factors in prevention of diseases related to elevated levels of Al in patients with kidney disorders that are being cured by dialysis processes.

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References

- [1] O.I. Egbuna, A. Bose, *Internet J. Nephrol.* 2 (2005) 1–8.
- [2] K. Berend, G.B. van der Voet, F.A. de Wolff, in: D.M.P. Mingos (Ed.), *Group 13 Chemistry II—Biological Aspects of Aluminum*, vol. 104, Springer, Berlin, 2002, pp. 1–58.
- [3] H.E. Witters, *Ecotoxicol. Environ. Saf.* 41 (1998) 90–95.
- [4] G. Berthon, *Coord. Chem. Rev.* 149 (1996) 241–280.
- [5] *European Pharmacopeia*, third ed., Council of Europe, Strasbourg, 1997, p. 1540–1542.
- [6] L.M. de Carvalho, P.C. do Nascimento, D. Bohrer, R. Stefanello, D. Bertagnolli, *Anal. Chim. Acta* 546 (2005) 79–84.
- [7] S. Knežević, R. Milačić, M. Veber, *Fresenius J. Anal. Chem.* 362 (1998) 162–166.
- [8] A. Martín-Esteban, P. Fernández, C. Pérez-Conde, A. Gutiérrez, C. Cámara, *Anal. Chim. Acta* 304 (1995) 121–126.
- [9] D. Bohrer do Nascimento, G. Schwedt, *Mikrochim. Acta* 126 (1997) 159–166.
- [10] D. Bohrer, A. Gioda, R. Binotto, P.C. do Nascimento, *Anal. Chim. Acta* 362 (1998) 163–169.
- [11] P.C. Nascimento, C.L. Jost, M.V. Guterres, L.D. Del’ Fabro, L.M. de Carvalho, D. Bohrer, *Talanta* 70 (2006) 540–545.
- [12] F. Hernandez Hernandez, J. Medina Escriche, *Analyst* 109 (1984) 1585–1588.
- [13] M.A. Raggi, G. Varani, V. Cavrini, D. Lacche, L. Nobile, *Anal. Lett.* 19 (1986) 1435–1441.
- [14] M.A. Raggi, R. Mandrioli, C. Sabbioni, F. Bugamelli, G. Cantelli Forti, *Eur. J. Pharm. Sci.* 6 (1998) S45–S48.
- [15] M.A. Raggi, C. Sabbioni, G. Cantelli Forti, *J. Pharm. Biomed. Anal.* 21 (2000) 1191–1196.
- [16] M. Buratti, C. Valla, O. Pellegrino, F.M. Rubino, A. Colombi, *Anal. Biochem.* 353 (2006) 63–68.
- [17] P. Fernández, C. Pérez Conde, A. Gutiérrez, C. Cámara, *Talanta* 38 (1991) 1387–1392.
- [18] Z. Li, N. Lu, X. Zhou, Q. Song, *J. Pharm. Biomed. Anal.* 43 (2007) 1609–1614.
- [19] C. Locatelli, *Electroanalysis* 15 (2003) 1397–1402.
- [20] P.L. Trentini, M. Ascanelli, B. Zanforlini, F. Venturini, G. Bucci, F. Fagioli, *J. Anal. At. Spectrom.* 8 (1993) 905–909.
- [21] M.R. Pereiro García, A. López García, M.E. Diaz Garcia, A. Sanz-Medel, *J. Anal. At. Spectrom.* 5 (1990) 15–19.
- [22] J. Smeyers-Verbeke, D. Verbeelen, *Anal. Chem.* 60 (1988) 380–383.
- [23] A.D. Woolfson, G.M. Gracey, *Analyst* 112 (1987) 1387–1389.
- [24] L. Ljunggren, I. Altréll, L. Risinger, G. Johansson, *Anal. Chim. Acta* 256 (1992) 75–80.
- [25] M.R. Pereiro García, M.E. Diaz Garcia, A. Sanz-Medel, *Analyst* 115 (1990) 575–579.
- [26] J.L. Rodrigues, C.S. de Magalhaes, P.O. Luccas, *J. Pharm. Biomed. Anal.* 36 (2005) 1119–1123.