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# Optimisation of parameters for determination of rubidium in spent CAPD fluids by flame and electrothermal atomic absorption spectrometry

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**Abstract**

An analytical procedure is reported for the determination of rubidium in spent continuous ambulatory peritoneal dialysis (CAPD) fluids by flame and electrothermal atomic absorption spectrometry (FAAS, ETAAS). Samples of spent CAPD fluids were collected as 5 ml aliquots in polyethylene tubes and stored in a freezer at $-20$°C. Before analysis, samples were equilibrated to room temperature and analysed within 8 h. A total of 2 mg $ml^{-1}$ of caesium was added to each sample and standard solution to overcome interferences from ionisation. An air–acetylene flame was applied in FAAS determinations. Analysis was performed against aqueous standards. The calibration graph was linear from 30.0 up to 5000 μg $l^{-1}$ Rb, while the limit of detection (3 s) was found to be 20.0 μg $l^{-1}$ rubidium. Good repeatability of measurement (RSD 1%) was obtained. Parameters were also optimised for determination of rubidium in spent CAPD fluids by ETAAS. Ten-fold diluted samples (3.5% nitric acid) were analysed applying standard addition calibration. The calibration graph was linear from 2.0 up to 30.0 μg $l^{-1}$ rubidium, while the limit of detection (3 s) was found to be 1.0 μg $l^{-1}$ rubidium (sample volume 10 μl). Good repeatability of measurement (RSD 5%) was obtained. The results of direct determination by FAAS and ETAAS were compared to those obtained after acid digestion of samples in Parr bombs. The accuracy of the procedure for direct determination was checked by spiking samples. In 73% of samples analysed, the differences between the results obtained by the two techniques, either for direct determinations of samples or for samples digested in a Parr bomb did not exceed $\pm 10$%. 

*Keywords:* Rubidium determination; Flame and electrothermal atomic absorption spectrometry; Direct determination and acid digestion in a Parr bomb; Spent CAPD fluids

## 1. Introduction

Trace elements play an important role in a health status of dialysis patients. It is well known that some trace elements may be accumulated in

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the body, while others may be depleted [1]. Aluminium has been the most intensively investigated due to its extremely toxic health effects. Even at a slightly elevated body burden via dialysis fluid or by ingestion of aluminium containing drugs, it may induce anaemia [2], aluminium related bone diseases [3], and encephalopathy [4]. Chromium may also accumulate in the body via the dialysis fluid [1,5]. There are reports that silicon [5] and strontium levels [1,5] are also increased in patients with chronic renal failure. In contrast, concentrations of selenium [5,6] bromine and rubidium are decreased in the blood of dialysis patients [1,7,8]. It is reported that depletion of rubidium is possibly related to disturbances of the nervous system of dialysis patients [1]. In order to estimate the role of rubidium in renal patients, clinical samples should be analysed. Rubidium was examined in whole blood [9,12,14], plasma [9,11–13], serum [10,14,16,17], red cells [9–11], human semen [15] and urine [13,14]. There is also a report on determination of rubidium in fresh CAPD fluids [18], but there are few data available on determination of rubidium in spent CAPD fluids. Analyses of rubidium were made by neutron activation analysis (NAA) [10,14–18], AAS [13], flame emission [9] and ETAAS [11,12]. NAA offers good sensitivity for rubidium and the possibility of simultaneous determination of a great number of other elements. However, it is very expensive and not widely available. Although AAS is a much cheaper and also suitable analytical method for determination of trace elements, it was not frequently applied in analysis of rubidium in clinical samples. Since the technique is liable to matrix interference effects, parameters should be carefully optimised for reliable determination of rubidium in complex matrices such us biological materials.

The aim of our work was to optimise the analytical procedure and measurement parameters for the determination of rubidium in spent CAPD fluids by FAAS and ETAAS. Results of direct determinations were compared to those obtained after acid digestion of sample in a Parr bomb. The accuracy of the procedure for direct determination by FAAS and ETAAS was checked by spiking of samples. On the basis of the analytical data an evaluation was made whether rubidium depletion in CAPD patients is possibly related to its loss through the peritoneal membrane during dialysis treatment.

## 2. Materials and methods

### 2.1. Instrumentation

Rubidium was determined by FAAS on a Varian Spectra AA 110 atomic absorption spectrometer in an air–acetylene flame, and by ETAAS on a Hitachi Z-8270 polarized Zeeman atomic absorption spectrophotometer equipped with an autosampler.

### 2.2. Reagents

Merck Suprapur acids and water doubly distilled in quartz were used for cleaning of laboratory ware and preparation of standard solutions. All other chemicals were of analytical reagent grade.

A stock standard rubidium solution ($1000 \pm 2$ mg Rb $l^{-1}$ as $Rb_2CO_3$ in 5% $HNO_3$) was obtained from Merck.

A stock standard caesium solution ($50 \pm 0.1$ g Cs $l^{-1}$) was used as an ionisation buffer. It was prepared by dissolving 63.359 g CsCl (Merck) in 1000 ml of water.

Working standards of rubidium were prepared by dilution of the stock solution with water and addition of an appropriate amount of caesium, so that the final concentration was 2 g Cs $l^{-1}$.

### 2.3. Sample preparation

Samples of spent CAPD fluids with various contents of glucose (1.36, 2.27 and 3.86%) were collected after CAPD fluid exchange in 5 ml polyethylene tubes and stored in a freezer at $-20$°C. Before analysis samples were equilibrated to room temperature and analysed within 8 h. Direct analyses were done by FAAS and ETAAS. For comparative analysis 4.0 ml of sample was digested with 1.0 ml of 65% nitric acid in a Parr bomb at 180°C for 12 h. To standard solution and each sample 2 g $l^{-1}$ of caesium was added to overcome interferences from ionization.

## 3. Results and discussion

### 3.1. Optimisation of measurement parameters for determination of rubidium in spent CAPD fluids by FAAS

Rubidium in spent CAPD fluids was determined in an air–acetylene flame at 780.0 nm. At this wavelength, non-specific absorption does not contribute to the atomic absorption signal, so background was not corrected. To compensate interferences arising from ionisation and to obtain a linear calibration curve, 2 g $l^{-1}$ of Cs was added to each sample and standard solution. For the same reason Allain et al. [9] recommended the addition of caesium in analysis of rubidium in blood samples by flame emission spectrometry. It was found experimentally that the sample matrix does not influence the sensitivity of measurement in the determination of rubidium by FAAS. The same results for the samples analysed were obtained when aqueous standard solutions or a standard addition calibration were applied. For that reason, determination of rubidium in the samples of spent CAPD fluids by FAAS was performed against aqueous standards.

### 3.2. Calibration graph, limit of detection and repeatability of measurements of rubidium by FAAS

The calibration graph for aqueous standard solutions was proved to be linear from 30.0 to 5000 μg $l^{-1}$ of rubidium with a correlation coefficient better than 0.9990. The limit of detection (LOD) calculated on a 3 s basis (a value of three times the standard deviation of the blank) was found to be 20.0 μg $l^{-1}$ of rubidium. The repeatability of measurement (RSD) was tested in one representative sample of spent CAPD fluid by six parallel determinations. It was found to be $\pm$ 1.0% either for digested samples or for direct FAAS determinations.

### 3.3. Comparative analysis of rubidium in spent CAPD fluids after acid digestion and by direct determination employing FAAS

The results of direct determination by FAAS were compared to those obtained after acid digestion of sample in a Parr bomb. The accuracy of the procedure for direct determination was checked by spiking of samples with 100 μg $l^{-1}$ of rubidium. Results are presented in Table 1. The data indicate that in 61% of the samples analysed, differences between the results obtained after acid digestion and by direct determination of rubidium employing FAAS do not exceed $\pm$ 5%, and for the majority of other samples analysed $\pm$ 15%. It is also evident from the data of Table 1 that in 95% of samples analysed, the recoveries for spiked samples lie between 98 and 102%. On the basis of these observations (Table 1), it can be concluded that reliable determination of rubidium in spent CAPD fluids can be performed by FAAS when the recommended analytical procedure is applied.

### 3.4. Optimisation of measurement parameters for determination of rubidium in spent CAPD fluids by ETAAS

Samples of spent CAPD fluids were diluted before analysis in order to determine rubidium in the linear concentration range and to reduce matrix effects due to the presence of proteins. Ten-fold dilution with 3.5% nitric acid gave reproducible measurements. A total of 2 g $l^{-1}$ of caesium was added to each sample and standard solution to compensate interference effects due to ionisation. The standard addition method was applied in the calibration procedure. A total of 10 μl of sample was injected into the pyrolitically coated graphite tube and carefully dried by a slow temperature ramp to 140°C. To prevent a loss of rubidium atoms during the ashing step, the ashing temperature for rubidium should not exceed 600°C. Although at this temperature the matrix is not completely removed, non-specific absorption does not contribute to the atomisation signal at 780.0 nm. Therefore, there is no need for the use of matrix modifiers. The measurement parameters for the determination of rubidium in spent CAPD fluids by ETAAS are presented in Table 2.

### 3.5. Calibration graph, limit of detection and repeatability of measurements of rubidium by ETAAS

The calibration graph for aqueous standard

solutions was linear from 2.0 to 30.0 μg $l^{-1}$ of rubidium, with correlation coefficient better than 0.9990. The limit of detection (LOD) calculated on a 3 s basis was found to be 1.0 μg $l^{-1}$ of rubidium. The repeatability of measurement (RSD) was tested in one representative sample of spent CAPD fluid by six parallel determinations. It was found to be better than ± 5.0% either for digested samples or for direct ETAAS determinations.

Table 1
Comparative analysis* of rubidium in spent CAPD fluids after acid digestion and by direct determination employing the FAAS technique, and the recoveries in spiked samples for direct determination by FAAS

| Sample no. | Acid digestion (μg $l^{-1}$) | Direct determination (μg $l^{-1}$) | Rb added (μg $l^{-1}$) | Rb found (μg $l^{-1}$) | Recovery (%) |
|---|---|---|---|---|---|
| 1/1.36% Glc | 45 ± 1 | 48 ± 1 | 100 ± 1 | 147 ± 2 | 99.0 |
| 2/1.36% Glc | 43 ± 1 | 53 ± 1 | 100 ± 1 | 150 ± 2 | 98.0 |
| 3/1.36% Glc | 105 ± 1 | 109 ± 1 | 100 ± 1 | 211 ± 2 | 101.0 |
| 4/1.36% Glc | 113 ± 1 | 118 ± 1 | 100 ± 1 | 215 ± 2 | 98.5 |
| 5/1.36% Glc | 107 ± 1 | 109 ± 1 | 100 ± 1 | 207 ± 2 | 99.0 |
| 6/1.36% Glc | 93 ± 1 | 99 ± 1 | 100 ± 1 | 195 ± 2 | 98.0 |
| 7/2.27% Glc | 101 ± 1 | 100 ± 1 | 100 ± 1 | 192 ± 2 | 96.0 |
| 8/2.27% Glc | 84 ± 1 | 74 ± 1 | 100 ± 1 | 171 ± 2 | 98.0 |
| 9/2.27% Glc | 63 ± 1 | 67 ± 1 | 100 ± 1 | 164 ± 2 | 98.0 |
| 10/2.27% Glc | 106 ± 1 | 108 ± 1 | 100 ± 1 | 207 ± 2 | 99.5 |
| 11/2.27% Glc | 75 ± 1 | 75 ± 1 | 100 ± 1 | 172 ± 2 | 98.5 |
| 12/2.27% Glc | 81 ± 1 | 95 ± 1 | 100 ± 1 | 178 ± 2 | 95.0 |
| 13/3.86% Glc | 73 ± 1 | 71 ± 1 | 100 ± 1 | 173 ± 2 | 101.0 |
| 14/3.86% Glc | 75 ± 1 | 92 ± 1 | 100 ± 1 | 192 ± 2 | 100.0 |
| 15/3.86% Glc | 68 ± 1 | 67 ± 1 | 100 ± 1 | 168 ± 2 | 100.5 |
| 16/3.86% Glc | 62 ± 1 | 57 ± 1 | 100 ± 1 | 154 ± 2 | 98.0 |
| 17/3.86% Glc | 56 ± 1 | 54 ± 1 | 100 ± 1 | 151 ± 2 | 102.0 |
| 18/3.86% Glc | 54 ± 1 | 58 ± 1 | 100 ± 1 | 155 ± 2 | 98.0 |

* Results are expressed as the mean of three parallel determinations ± standard deviation of measurement.

Table 2
Measurement parameters for determination of rubidium in spent CAPD fluids by ETAAS with Zeeman background correction[a]

| Electrothermal atomization programme | | | | | | |
|---|---|---|---|---|---|---|
| Stage no. | Stage | Temp. (°C) Start | Temp. (°C) End | Time (s) Ramp | Time (s) Hold | Gas flow (ml $min^{-1}$) |
| 1 | Dry | 60 | 90 | 10 | 0 | 200 |
| 2 | Dry | 90 | 100 | 10 | 5 | 200 |
| 3 | Dry | 100 | 140 | 10 | 5 | 200 |
| 4 | Ash | 140 | 600 | 10 | 15 | 100 |
| 5 | Atomization | 2000 | 2000 | 0 | 4 | 0 |
| 6 | Clean | 2800 | 2800 | 0 | 7 | 200 |
| 7 | Cool | – | – | 0 | 5 | 200 |

[a] Wavelength, 780.0 nm; spectral bandwidth, 0.40 nm; lamp current, 15.0 mA; sample volume, 10 μl.

Table 3
Comparative analysis* of rubidium in spent CAPD fluids after acid digestion and by direct determination employing the ETAAS technique, and the recoveries in spiked samples for direct determination by ETAAS, $n = 3$

| Sample no. | Acid digestion ($\mu g\ l^{-1}$) | Direct determination ($\mu g\ l^{-1}$) | Rb added ($\mu g\ l^{-1}$) | Rb found ($\mu g\ l^{-1}$) | Recovery (%) |
|---|---|---|---|---|---|
| 1/1.36% Glc | $58 \pm 3$ | $58 \pm 3$ | $100 \pm 1$ | $158 \pm 2$ | 100.0 |
| 2/1.36% Glc | $43 \pm 2$ | $56 \pm 1$ | $100 \pm 1$ | $159 \pm 2$ | 101.0 |
| 3/1.36% Glc | $116 \pm 2$ | $117 \pm 2$ | $100 \pm 1$ | $229 \pm 5$ | 101.0 |
| 4/1.36% Glc | $118 \pm 2$ | $125 \pm 3$ | $100 \pm 1$ | $222 \pm 5$ | 98.5 |
| 5/1.36% Glc | $110 \pm 2$ | $116 \pm 4$ | $100 \pm 1$ | $216 \pm 5$ | 100.0 |
| 6/1.36% Glc | $105 \pm 2$ | $100 \pm 2$ | $100 \pm 1$ | $206 \pm 4$ | 103.0 |
| 7/2.27% Glc | $99 \pm 4$ | $101 \pm 1$ | $100 \pm 1$ | $198 \pm 5$ | 98.5 |
| 8/2.27% Glc | $84 \pm 4$ | $96 \pm 2$ | $100 \pm 1$ | $215 \pm 5$ | 109.5 |
| 9/2.27% Glc | $65 \pm 3$ | $75 \pm 3$ | $100 \pm 1$ | $183 \pm 3$ | 104.5 |
| 10/2.27% Glc | $125 \pm 5$ | $132 \pm 2$ | $100 \pm 1$ | $229 \pm 3$ | 98.5 |
| 11/2.27% Glc | $99 \pm 2$ | $100 \pm 2$ | $100 \pm 1$ | $202 \pm 6$ | 101.0 |
| 12/2.27% Glc | $95 \pm 3$ | $93 \pm 3$ | $100 \pm 1$ | $205 \pm 4$ | 101.0 |
| 13/3.86% Glc | $76 \pm 2$ | $76 \pm 3$ | $100 \pm 1$ | $176 \pm 2$ | 100.0 |
| 14/3.86% Glc | $80 \pm 4$ | $79 \pm 2$ | $100 \pm 1$ | $181 \pm 2$ | 101.0 |
| 15/3.86% Glc | $58 \pm 1$ | $69 \pm 1$ | $100 \pm 1$ | $179 \pm 3$ | 100.0 |
| 16/3.86% Glc | $62 \pm 1$ | $55 \pm 1$ | $100 \pm 1$ | $150 \pm 2$ | 97.0 |
| 17/3.86% Glc | $54 \pm 2$ | $55 \pm 1$ | $100 \pm 1$ | $150 \pm 2$ | 96.5 |
| 18/3.86% Glc | $52 \pm 1$ | $59 \pm 1$ | $100 \pm 1$ | $157 \pm 2$ | 99.0 |

* Results are expressed as the mean of three parallel determintions $\pm$ standard deviation of measurement.

### 3.6. Comparative analysis of rubidium in spent CAPD fluids after acid digestion and by direct determination employing ETAAS

The results of direct determination by ETAAS were compared to those obtained after acid digestion of sample in a Parr bomb. The accuracy of the procedure for direct determination was checked by spiking of samples with 100 $\mu g\ l^{-1}$ of rubidium. Results are presented in Table 3. The data indicate that in 56% of the samples analysed differences between the results obtained after acid digestion and by direct determination of rubidium employing ETAAS do not exceed $\pm 5\%$, and for the majority of other samples analysed $\pm 15\%$. It is also evident from the data of Table 3 that in 95% of samples analysed the recoveries for spiked samples lie between 98 and 104%. On the basis of these observations (Table 3) it can be concluded that reliable determination of rubidium in spent CAPD fluids can also be performed by ETAAS when the recommended analytical procedure is applied.

### 3.7. Determination of rubidium in fresh CAPD fluids

In all samples of spent CAPD fluids analysed, rubidium was also determined in the corresponding fresh CAPD fluids. For that purpose, direct ETAAS analyses were performed under the recommended measurement parameters. The concentrations of rubidium in fresh CAPD fluids were found to be below 1.0 $\mu g\ l^{-1}$.

### 3.8. Comparison of data obtained by the two analytical techniques for determination of rubidium in CAPD fluids

On the basis of the data in Tables 1–3, it is evident that good agreement is obtained between FAAS and ETAAS techniques for determination of rubidium in spent CAPD fluids. In 73% of samples analysed, differences between the results obtained by the two techniques, either for direct determination or for samples digested in a Parr bomb, do not exceed $\pm 10\%$. The concentrations

of rubidium in spent CAPD fluids ranged between 50 and 130 μg $l^{-1}$, while the concentrations of rubidium in fresh CAPD fluids were below 1.0 μg $l^{-1}$. Since FAAS is a simple and rapid technique it is recommended for determination of rubidium in spent CAPD fluids. ETAAS, which is more sensitive, is a convenient method for determination of rubidium in fresh CAPD fluids. It can also be applied in speciation of rubidium in biological samples.

The data from the present study indicate loses of rubidium through the peritoneum during the dialysis process, which may be of clinical importance for the health status of CAPD patients.

## 4. Conclusion

An analytical procedure and the associated measurement parameters were optimised for the reliable determination of rubidium in spent CAPD fluids by FAAS and ETAAS. Comparison of the results of direct determinations with those obtained after acid digestion indicated good agreement between the two techniques, the differences in general not exceeding $\pm 10\%$. The procedure for direct determination of spent CAPD fluids was validated by spiking of samples. The recoveries for spiked samples ranged between 98 and 104% for both techniques. Because of the simplicity of the procedure, direct determination is recommended for the analysis of CAPD fluids. The concentrations of rubidium in spent CAPD fluids ranged between 50 and 130 μg $l^{-1}$, while the concentrations of rubidium in fresh CAPD fluids were below 1.0 μg $l^{-1}$. Since FAAS is a simple and rapid technique, it is a convenient method for the determination of rubidium in spent CAPD fluids, while the more sensitive ETAAS technique is recommended for determination of rubidium in fresh CAPD fluids. The data of the present study indicate losses of rubidium through the peritoneal membrane during the peritoneal dialysis, which may be of clinical importance for the health status of CAPD patients.

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