DETERMINATION OF TRACE CONCENTRATIONS OF COPPER BY FIA–FAAS AFTER PRECONCENTRATION ON CHELATING SORBENTS

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A FIA–FAAS apparatus containing a six-channel sorption equipment with five 3 × 26 mm microcolumns packed with Spheron Oxin 1 000, Ostsorb Oxin and Ostsorb DTTA was set up. Combined with sorption from 0·002M acetate buffer at pH 4·2 and desorption with 2M-HCl, copper can be determined at concentrations up to 100, 150 and 200 $\mu g\, l^{-1}$, respectively. For sample and eluent flow rates of 5·0 and 4·0 ml min^{-1}, respectively, and a sample injection time of 5 min, the limit of copper determination is $L_Q = 0{\cdot}3\ \mu g\, l^{-1}$, repeatability s_r is better than 2% and recovery is $R = 100 \pm 2\%$. The enrichment factor is on the order of 10^2 and is a linear function of time (volume) of sample injection up to 5 min and of the sample injection flow rate up to 11 ml min^{-1} for Spheron Oxin 1 000 and Ostsorb DTTA. For times of sorption of 60 and 300 s, the sampling frequency is 70 and 35 samples/h, respectively. The parameters of the FIA–FAAS determination (acetylene–air flame) are comparable to or better than those achieved by ETA AAS. The method was applied to the determination of traces of copper in high-purity water.

Flow injection analysis (FIA) combined with flame atomic absorption spectroscopy (FAAS) has several assets particularly in analytical procedures which include sample separation and preconcentration treatment. The entire procedure can easily be partly or completely automated.

Very convenient is the preconcentration and separation of analyte or removal of the sample matrix on a microcolumn packed with a chelating sorbent. The determination limit by flame AAS can be thereby lowered to levels commonly attained by AAS with electrothermal atomization (ETA AAS) while the instrumentation remains considerably simpler and less expensive.

Several papers[1–7] have dealt with the preconcentration of metal ions in FIA–FAAS using chelating sorbents with functional groups of iminodiacetic acid, 8-quinolinol, salicylic acid and other analytical functional groups. The ions are sorbed in the free form on cation exchangers or in the form of their chloro complexes on anion exchangers. The sensitivity, precision, selectivity and recovery of the determination are affected by the kinetics of sorption and, in particular, desorption of the charged species and stability of their bonding to the chelating groups[1–7].

The dynamic properties of chelating sorbents depend on a number of factors, whereby their applicability can be affected appreciably. Among the most important, in addition to the type of matrix, particle size and kind of chelating analytical functional groups, are the availability of these groups, dynamic break-through-capacity and selectivity[8].

In the work described in this paper, a FIA–FAAS apparatus was set up for the determination of copper after its preconcentration on microcolumns packed with chelating sorbents. The properties of the Czechoslovak commercial sorbents Spheron Oxin 1 000, Ostsorb Oxin and Ostsorb DTTA, with 8-quinolinol or diethylenetriaminetetraacetic acid functional groups bonded to glycol methacrylate or cellulose macroporous matrices, were compared. A FIA–FAAS procedure was worked out for the determination of trace concentrations of copper in high-purity water.

EXPERIMENTAL

Chemical and Apparatus

Standard solution of copper(II) in a concentration of $\varrho_{Cu} = 953$ mg l^{-1} in 0·1M-HNO_3 was prepared by dissolving copper metal (99·96%) in nitric acid. The solution was standardized by chelometric titration with EDTA using murexide as the indicator. Working solutions were prepared by dilution of this standard solution with 0·1M-HNO_3. Acetate buffer ($c_{Ac} = 0{\cdot}2$ mol . l^{-1}), pH 4·2 or 5·4, was prepared from acetic acid and sodium acetate. The other chemicals and solvents were commercial samples (Lachema, Brno) of p.a. or p.p. (HCl, HNO_3) purity.

Spheron Oxin 1 000 (Lachema, Brno) is a chelating sorbent with 8-quinolinol functional groups bonded via side chains to a glycol methacrylate gel of a defined porosity (pore volume 1·25 to 1·5 ml g^{-1}) with stationary sorption capacity 0·25—0·30 mmol g^{-1} and particle diameter 40—63 or 63—100 μm.

Ostsorb Oxin and Ostsorb DTTA (Spolchemie, Ústí nad Labem) are chelating sorbents with 8-quinolinol and diethylenetriaminetetracetic acid functional groups, respectively, bonded to side chains of macroporous pearl cellulose of high porosity (pore volume 5·0—5·5 ml g^{-1}), sorption capacity in stationary conditions 0·5 and 0·6 mmol g^{-1}, respectively, and diameters of the spherical particles 0·1 to 0·5 mm. The two sorbents were stored in a liquid medium to avoid irreversible changes in porosity on drying and reswelling.

All sorbents were packed into microcolumns in the form of their aqueous suspensions. Prior to use, the microcolumns were washed repeatedly with 2M-HCl and water to remove manufacture impurities if present.

Measurements were performed on a PE 306 atomic absorption spectrometer in the acetylene–air flame at flow rates of 3·6 and 22·5 l min^{-1}, respectively, using a 10 cm slot burner and applying a nebulizer aspiration rate of 6·2 ml min^{-1}, or on a PE 3 030 atomic absorption spectrometer with an HGA 400 electrothermal atomizer and an AS 1 automatic injector (all Perkin–Elmer, Norwalk, U.S.A.) at the following parameters: drying at 150°C for 30 s, decomposition at 800°C for 20 s, atomization at 2 600°C for 6 s, atomization temperature increase in 1 s. Argon flow rate was 50 ml min^{-1}. An Intensitron hollow cathode lamp (Cu) (Perkin–Elmer) was used as the monochromatic radiation source at the 324·7 nm resonance line; slit width 0·7 nm, heating current 15 and 12 mA for the PE 306 and PE 3 030 instruments, respectively.

Analytical signals were recorded on a TZ 4 100 recorder (Laboratorní přístroje, Praha). Concentrations of copper were evaluated based on peak height or area measurements.

The FIA–FAAS apparatus included two S-32 peristaltic pumps (Domet, Poland), alllowing the flow rate to be continuously adjusted over the 0·1—11·5 ml min^{-1} region. A Unipan 304 (Zalimp, Poland) five-channel peristaltic pump, with flow rates adjustable stepwise from 0·1 to 18 ml min^{-1}, served for the sample and washing liquid delivery in measurements with the six--channel five-column sorption equipment. Eluting solution and washing liquid were fed through Tygon tubes 3 mm i.d. (Technicon, U.S.A.); for sample delivery, these tubes were lined with thin-walled Teflon capillaries 1 mm i.d. (Norton Chemoplast, Wayne, U.S.A.).

Microlitre volumes of Cu(II) samples were injected by means of a loop injector with variable loop volumes $V_l > 10$ µl. A laboratory stopwatch was used when determining the preconcentration times and sample volumes based on known flow rates. Teflon capillaries 0·3 or 0·6 mm i.d. (Norton Chemplast, Wayne, U.S.A.) served for liquid transport.

The FIA parameters were optimized on a simple one-channel equipment[1]. The breakthrough capacity of the packed microcolumns was measured on a one-channel FIA apparatus; microcolumns 3 × 20 mm packed with Spheron Oxin 1 000 (volume 140 µl, 50 mg packing; Column A) or 3 × 26 mm packed with 185 µl of Ostsorb Oxin (Column B) or Ostsorb DTTA (Column C) were employed.

Copper solution in 0·002M acetate buffer at pH 4·2 was injected on the microcolumns by means of an S-32 peristaltic pump at a flow rate of 5 ml min^{-1}; 1·0, 0·5 or 0·25 ml eluate fractions were collected in polystyrene vessels of a fraction collector. The concentration of copper in the fractions was determined by injecting 20 µl volumes into the HGA 400 electrothermal atomizer. Occasionally, the eluate was nebulized into the acetylene–air flame directly from the fraction collector vessels.

The trace concentrations of copper after preconcentration on the chelating sorbents were determined using a six-channel sorption equipment (Fig. 1) with five microcolumns, which is a modification of the device after Schultze and Elsholz[4]. The device consists of a pair of stators with inlet and outlet capillaries for liquid feed, and a rotor with five 3 M 26 mm sorption microcolumns and a free 0·6 × 26 mm microchannel. The rotor and the two stators were centrally located on a pin and were pushed together at their highly polished faces by a spring.

Copper solutions were injected on the packed microcolumns C1—C5 by means of the pump P5 from sample reservoirs. While the Cu(II) ions were sorbed, the solution with the matrix was drained into the waste W. At the same time, the peristaltic pump P1 delivered water to the nebulizer via the microchannel EC. After injection of the desired sample volume, defined by the flow rate and time of injection, the microcolumns were washed for 20 s with water or with 0·002M acetate buffer at pH 4·2.

By stepwise 60° turning of the rotor, the microcolumns C1 through C5 were in turn positioned in the stream of the eluting solution (2M-HCl), which was pumped for 15 s at a flow rate of $F_E = 4$ ml min^{-1} by means of the peristaltic pump P1. The eluting solution streamed in the counter-current mode with respect to the sample flow on the microcolumn in the sorption cycle. The Cu(II) ions sorbed were eluted and fed directly into the FAAS nebulizer through a 0·6 × × 70 mm Teflon capillary. The analytical signal was recorded.

After elution, the microcolumns C1—C5 were in turn washed with water and thereby regenerated (see below). The sorption equipment with the peristaltic pumps P5 and P1 were operated manually following a time schedule, such as that shown in Fig. 2 for sample injection for 60 s, microcolumn washing for 20 s and elution of the microcolumns for 15 s each.

Unless stated otherwise, the sample injection rate was $F_S = 5{\cdot}0$ ml min^{-1}, acetate buffer concentration $c_{Ac} = 2$ mmol l^{-1} at pH 4·2, and eluting agent (2M-HCl) flow rate $F_E = 4{\cdot}0$ ml . . min^{-1}. The 3 × 26 mm microcolumns of the sorption apparatus were packed with 70 mg of

Spheron Oxin 1 000 (grain size 63—100 μm; Column D) or 185 μl of Ostsorb Oxin or Ostsorb DTTA (Columns B and C, respectively). The sample injection time was largely 60 s, only for copper concentrations below 10 μg l^{-1} this time was extended to 300 s.

The limit of determination was calculated as the concentration of copper corresponding to the analytical signal $A = \bar{A}_b + 10s_0$, where $\bar{A}_b$ is the arithmetic mean and s_0 the standard deviation of the analytical signal of the blank, obtained from 10 independent measurements. The repeatability of determination was defined by the relative standard deviation s_r of the average analytical signal, also for 10 independent measurements.

RESULTS AND DISCUSSION

Microcolumn Breakthrough Capacity

The criterion of breakthorugh of Cu(II) ions was the attaining of 1% of the analytical signal value in the given fraction of the passed Cu(II) solution at concentrations of ϱ_{Cu} = 200 μg l^{-1} for Spheron Oxin 1 000 or 100 μg l^{-1} for the Ostsorb sorbents. This signal was invariably related to the analytical signal of the copper solution in the acetate buffer (200 or 100 μg l^{-1}) obtained on the continuous direct nebulization at a flow rate of F_S = 5 ml min^{-1}, in the steady state. The more sensitive ETA AAS technique was used for the determination of copper in the eluate fractions.

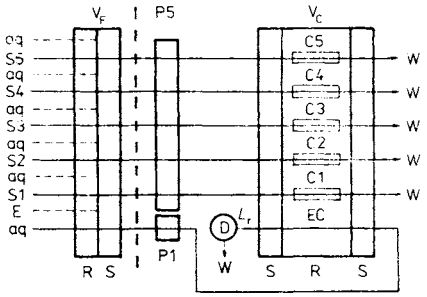

FIG. 1

FIA–FAAS apparatus. V_F switching valve, V_C six-way five-column injecting device, P5 five-channel peristaltic pump, P1 one-channel peristaltic pump, D FAAS detector, W waste, C1—C5 microcolumns (3 × 26 mm) packed with chelating sorbent, EC free microchannel 0·6 × 26 mm, R rotor, S stator, L_r reaction capillary (70 mm), S1—S5 samples 1—5, aq washing or regenerating liquid (water or 0·002M acetate buffer), E eluting agent (2M-HCl)

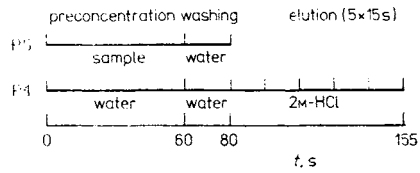

FIG. 2

Time schedule of measuring cycle with preconcentration (60 s), washing (20 s) and elution (5 × 15 s)

For Spheron Oxin 1000, grain size 63–100 or 40–63 μm, the breakthrough capacities found were $Q_{Cu} = 0{\cdot}57$ and $0{\cdot}63$ μmol g^{-1}, respectively. For the two cellulose-based chelating sorbents the breakthrough capacities, $Q_{Cu} = 0{\cdot}06$ and $0{\cdot}1$ μmol g^{-1}, respectively, were determined with higher errors because of the poor reproducibility of measurement of the blank. For Ostsorb Oxin, a 3% level of the steady-state analytical signal was attained when injecting 1 ml of the Cu(II) solution, and this value increased monotonically to approximately 12% for the 5 ml volume. Ostsorb DTTA exhibited a higher breakthrough capacity than Ostsorb Oxin; the 1% steady-state analytical signal level was obtained with approximately 2 ml of copper sample, and increased only slowly with increasing sample solution volume.

The copper sorption efficiency in such conditions was only 87 and 97% for Ostsorb Oxin and Ostsorb DTTA, respectively, as against the sorption on Spheron Oxin 1 000 which is extremely rapid and quantitative.

The breakthrough capacity of Column A (for the two grain sizes) decreases with the rate of injection of copper sample increasing over the region of $F_S = 0{\cdot}8$ to $4{\cdot}0$ ml min^{-1} at a constant concentration of $\varrho_{Cu} = 10$ mg l^{-1}, and with the concentration of copper in the solution increasing from 4 to 20 mg l^{-1} at a constant flow rate of $F_S = 2{\cdot}1$ ml min^{-1} (Fig. 3).

The flow rate of the Cu(II) solution controls the residence time of the ions in the microcolumn and, along with the metal ion concentration, affects significantly the sorption kinetics. At higher flow rates the metal ions are sorbed predominantly on the readily accessible chelating functional groups of the sorbent, whereby the breakthrough capacity is lowered. For all the sorbents, however, the absolute amount of ions retained in the same experimental conditions was constant and reproducible with $s_r \leqq 1\%$.

Optimization of Conditions of FIA–FAAS Determination

For the continuous injection of the copper solution with $\varrho_{Cu} = 100$ μg l^{-1} on Columns A or B for 60 s, the analytical signal in dependence on the flow rate of the eluting agent (2M-HCl) attained its maximum at $F_E = 4$ ml min^{-1}.

The different shape of the dependences over the entire region of flow rates F_E (Fig. 4) for Spheron Oxin and Ostsorb Oxin is presumably due to the more difficult desorption of the Cu^{2+} ions from the former as compared to the latter, because of the different nature of the sorbent matrices, porosity and particle size and shape, which are important parameters of the desorption kinetics.

This is also borne out by the peak shapes obtained for the two sorbents at $\varrho_{Cu} = 100$ μg l^{-1}; the peaks for Spheron Oxin 1000 are lower and more disperse, indicating a slower elution of the Cu^{2+} ions as compared to Ostsorb Oxin (peak height difference $\Delta h = 17\%$). On the other hand, the virtually identical peak areas

(difference $\Delta A = 3\%$) give evidence of quantitativeness of the elution from the two sorbents. Thus, the slower elution of Cu^{2+} ions from Spheron Oxin 1 000 is due to a poorer accessibility of the 8-quinolinol functional groups.

For the elution of the Cu(II) ions from Column A after sorption from a solution at $\varrho_{Cu} = 40\ \mu g\ l^{-1}$ for 60 s, the analytical signal is about 60% lower if the eluting agent (2M-HCl) is delivered continuously in the direction identical with that of the sample injection in the preconcentration cycle than in the counter-current mode. Whereas in the former case, the concentrated analyte zone passes through the entire microcolumn volume where it is dispersed on the sorbent particles, in the latter case the dispersion is minimal and, moreover, secondary concentration of the analyte zone by the eluting solution front takes place.

The analytical signal obtained with Spheron Oxin, 63–100 μm grain size, was virtually independent of the flow rate of the injected copper solution ($\varrho_{Cu} = 100\ \mu g\ .\ l^{-1}$) over the wide range of $F_S = 2{\cdot}5-9$ ml μmin^{-1}, and the sorption was quantitative (Fig. 5, curve *1*). At lower (below 2 ml min^{-1}) or higher (above 9 ml min^{-1}) flow rates the analytical signal decreased. In the former case this was due to a more

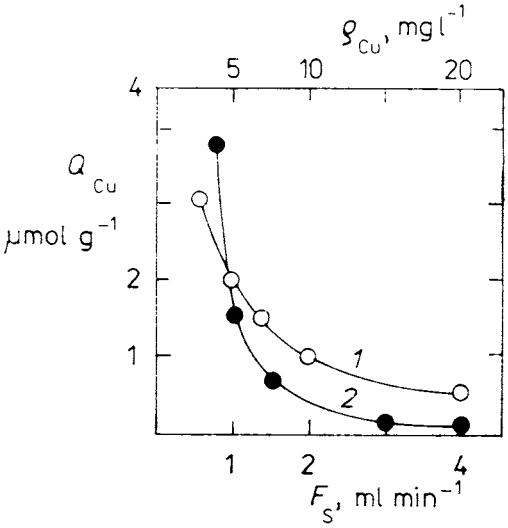

FIG. 3

Effect of sample injection flow rate (curve *1*) and concentration (curve *2*) on the breakthrough capacity of Columns A packed with Spheron Oxin; 0·002M acetate buffer, pH 4·2. Curve *1*: column 3 × 20 mm, grain size 63–100 μm, $\varrho_{Cu} = 10\ mg\ l^{-1}$. Curve *2*: column 2 × 50 mm, grain size 40–63 μm, flow rate of sample 2·1 ml min^{-1}

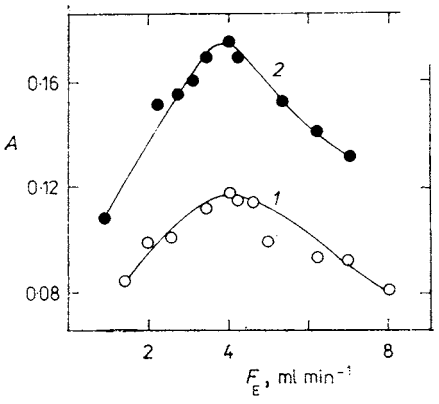

FIG. 4

Effect of flow rate of eluting agent (2M-HCl) on the analytical signal of sample sorbed on Spheron Oxin 1 000 (curve *1*) or Ostsorb Oxin (curve *2*) from solution at $\varrho_{Cu} = 100\ \mu g\ l^{-1}$ in 0·002M acetate buffer, pH 4·2. F_S (ml min^{-1}): *1* 5·2, *2* 5·4

difficult elution of the metal ions on the poorly accessible functional groups in the internal structure of the chelating sorbent, occurring to an increased extent at low sample injection flow rates when the residence time of the copper ions inside the sorbent structure is longer. This brings about broadening of the analyte zone, associated with a decreae in the peak height and increase in its width while the peak area remains constant. At high flow rates, the decrease in the analytical signal was due to a lowering in the breakthrough capacity of the microcolumn.

When using Ostsorb Oxin, with larger spherical particles, the analytical signal decreased monotonically over the entire region of F_S = 1 to 9 ml min^{-1} for copper concentration ϱ_{Cu} = 100 μg l^{-1} (Fig. 5, curve 2). This is due to the slower sorption kinetics and lower retention of the copper ions in the vicinity of the analytical functional groups of the sorbent. A value of F_S = 5·0 ml min^{-1}, ensuring a sufficiently rapid and quantitative sorption of copper ions, was chosen for practical applications.

The analytical signal obtained on injecting sample with ϱ_{Cu} = 100 μg l^{-1} for 60 or 300 s and eluting with 2M-HCl was unaffected by the time of washing the microcolumns with water or acetate buffer, by the time of their regeneration with these systems up to 60 s, or by the concentration of the acetate buffer up to 0·02 mol l^{-1} at pH 4·2.

The highest analytical signal in the above conditions was attained at pH 3–5 for Spheron Oxin 1000 and pH 3–5·5 for Ostsorb Oxin (Fig. 6). The pH 4·2 was chosen

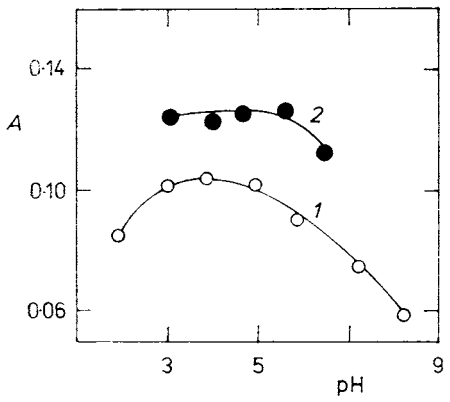

FIG. 5

Effect of sample flow rate F_S on the analytical signal for Spheron Oxin (curve 1) and Ostsorb Oxin (curve 2); ϱ_{Cu} = 100 μg l^{-1}, 0·002M acetate buffer, pH 4·2. F_E (ml min^{-1}): 1 4·2, 2 4·0

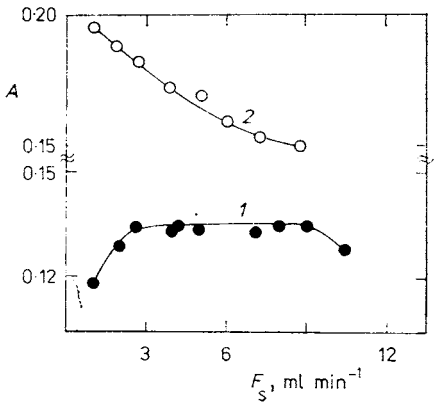

FIG. 6

Effect of pH on the efficiency of preconcentration of Cu(II) ions on columns packed with Spheron Oxin (curve 1) or Ostsorb Oxin (curve 2); ϱ_{Cu} = 100 μg l^{-1}, 0·002M acetate buffer, elution with 2M-HCl. F_S, F_E (ml min^{-1}): 1 5·0, 4·0; 2 5·2, 4·2

as optimum for the determination; the analytical signal then is independent of the acetate buffer concentration up to 0·02 mol l^{-1} and is equal to that for unbuffered solutions at pH ≈ 5. Since, however, increasing buffer concentrations bring about increase in the blank values, 0·002M acetate buffer was chosen for the measurements at pH 4·2.

The enrichment factor at $\varrho_{Cu} = 10\ \mu g\ l^{-1}$ increased linearly with the time of injection, i.e. with the total volume and the total amount of Cu^{2+} ions, over the entire region of 1–5 min for both Spheron Oxin 1000 and Ostsorb Oxin. Hence, by extending the time of sample injection, the enrichment factor, and thereby the determination limit, can be increased linearly, by approximately 50% per minute of injection.

An increase in the enrichment factor for the same frequency of sample injection can be also achieved by increasing the injection flow rate over the region of $F_S = 2-11$ ml min^{-1} at a constant time of injection of 60 s. For Spheron Oxin 1000, and to some degree also for Ostsorb DTTA, the dependence of the enrichment factor is linear, whereas for Ostsorb Oxin the slope of this dependence decreases monotonically. This decrease in the enrichment factor indicates a decrease in the breakthrough capacity at higher flow rates.

For the injection time of 60 s, the calibration curves are strictly linear up to $\varrho_{Cu} = 200\ \mu g\ l^{-1}$ using Ostsorb DTTA, 150 μg l^{-1} using Ostsorb Oxin, and only 100 μg l^{-1} using Spheron Oxin 1 000; at higher concentrations the slopes decrease. The wider linearity span achieved with Ostsorb DTTA (for the same sensitivity and limit of determination) is related with its somewhat higher breakthrough and sorption capacities as compared to Ostsorb Oxin; the different behavour of Spheron Oxin 1 000 is due to the different kinetics of desorption of Cu^{2+} ions, as mentioned above.

For the time of injection 300 s, the calibration curves are strictly linear up to $\varrho_{Cu} = 2\mu g\ l^{-1}$ for the three sorbents, the slopes being virtually identical. The determination limit is $L_Q = 0{\cdot}3\ \mu g\ l^{-1}$, repeatability of determination is $s_r < 2\%$ over the entire concentration region, the recovery is $R = 100 \pm 2\%$.

For the time-controlled calibration using a single solution, where the absolute amount of sample delivered was determined by the time of injection from 8 to 60 s at $\varrho_{Cu} = 100\ \mu g\ l^{-1}$ and $F_S = 5$ ml min^{-1}, the calibration plot of analytical signal vs time of injection was only linear for Ostsorb Oxin. The slope and statistical parameters of the calibration curve were identical those for the concentration region of $\varrho_{Cu} = 10-150\ \mu g\ l^{-1}$ when using a set of solutions with different concentrations at a constant time of injection. For Spheron Oxin 1 000, the calibration curves over the entire injection time region of 8–60 s were nonlinear, with decreasing slope values.

Time-controlled calibration with a single Cu(II) solution applying a variable time factor is faster and more convenient if the Cu(II) ions are preconcentrated from larger sample volumes. However, at shorter injection times and, hence, smaller total

volumes injected, it is rather difficult to exactly control the time schedule when operating the FIA injecting device manually. A considerable improvement in this respect can be achieved by the use of a microprocessor-controlled injector.

Application to Actual Samples

The FIA–FAAS method was applied to the determination of trace quantities of Cu(II) ions in the high-purity waters of power station cooling circuits. Microcolumn D, packed with Spheron Oxin 1 000, was used for preconcentration. Water samples were used unadjusted (resultant pH about 6) or adjusted with the acetate buffer, injection time was 5 or 15 min.

The recovery was verified on the above samples and on bidistilled water using a standard addition of Cu^{2+} ions corresponding to a concentration of 1 $\mu g\, l^{-1}$; it was $R = 100 \pm 2\%$ in all cases.

The concentrations found in the unbuffered and buffered solutions of water samples from the power station cooling circuit, $\varrho_{Cu} = 0{\cdot}38 \pm 0{\cdot}03$ and $0{\cdot}34 \pm 0{\cdot}04$ $\mu g\, l^{-1}$, respectively, agree well with the values obtained by ETA AAS ($\varrho_{Cu} < 0{\cdot}5$ $\mu g\, l^{-1}$), with the results obtained at the plant laboratory ($\varrho_{Cu} < 0{\cdot}5$ $\mu g\, l^{-1}$), and those obtained by FIA–FAAS with continuous liquid extraction ($\varrho_{Cu} = 0{\cdot}31 \pm 0{\cdot}03$ and $0{\cdot}33 \pm 0{\cdot}05$ $\mu g\, l^{-1}$, respectively). In bidistilled water, the concentration of copper was below the limit of determination even if the sorption time was extended to 15 min.

The comparison of the results of the various methods for the determination of Cu(II) ions gives evidence that the determination limit in the procedure where the Cu^{2+} ions are preconcentrated on a chelating sorbent microcolumn ($L_Q = 0{\cdot}3$ $\mu g\, l^{-1}$) is better than as obtained on the same apparatus and in the same conditions ($L_Q = 3{\cdot}3$ $\mu g\, l^{-1}$) using direct aspiration of Cu(II) solutions, and comparable to the limit of determination attained when employing liquid extraction in the FIA–FAAS determination of copper[9] ($L_Q = 2$ $\mu g\, l^{-1}$). It is, however, poorer than the limit of determination reached by ETA AAS with a direct delivery of the chelating sorbent with the preconcentrated analyte into the atomizer[10].

The time of a determination by ETA AAS is about 90 s, which corresponds to a sampling frequency of approximately 45 samples/h. When using the six-channel five-column sorption device, the time of a determination is about 50 or 100 s for injection times of 60 and 300 s, respectively, whereform the sampling frequency is 70 or 35 samples/h, respectively, hence, somewhat higher or lower, respectively, than in the ETA AAS treatment.

From among the chelating sorbents tested, Spheron Oxin 1 000 exhibits the highest sorption capactiy, and sorption on it is quantitative over wide regions of concentrations and flow rates. A drawback is in the narrower range of linearity of the calibration plots. The peak shapes are also different from those for the Ostsorb sorbents;

the analytical signal is lower and broader because of the slower elution of analyte, this effect being more marked at higher concentrations.

The calibration plots for Ostsorb Oxin and Ostosorb DTTA are linear up to $\varrho_{Cu} = 150$ and 200 $\mu g\, l^{-1}$, respectively. The peaks are narrower and higher than for Spheron Oxin 1 000, the sorption, however, is not quantitative, particularly at higher concentrations and/or higher flow rates. The desorption is rapid and quantitative. Ostsorb Oxin has a somewhat poorer breakthrough capacity than the two other sorbents.

At low copper concentrations, below 10 $\mu g\, l^{-1}$, the three sorbents tested are approximately equal in performance. The parameters of the method of determination at such concentrations are mutually identical to within the limits of experimental error. An asset of the pearl-cellulose-based sorbents as compared to Spheron Oxin 1 000 is their lower hydrodynamic resistance, which is probably due to the better homogeneity of the particle shape and size.

In conclusion, the data obtained suggest that the FIA–FAAS method including preconcentration on microcolumns of chelating sorbents can serve as an alternative to the ETA AAS technique for the determination of trace concentrations of copper.

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