Notes

7-Amino-4-azaheptyl Grafted onto a Silica Gel as a Sorbent for the On-line Preconcentration and Determination of Iron(III) in Water Samples

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A new sorbent was synthesized by anchoring 7-amino-4-azaheptyltrimetoxisilane, freshly prepared, to silica gel, producing 7-amino-4-azaheptyl anchored silica gel (AAHSG). This material was characterized by infrared spectroscopy (IR), elemental analysis (CHN), and nitrogen adsorption-desorption isotherms. Isotherms of the adsorption of Fe^{3+}, Fe^{2+} and Cu^{2+} on AAHSG were recorded, which indicated that Fe^{3+} presents a higher affinity by the sorbent. Therefore, AAHSG was successfully employed as a sorbent in a simple flow system for the preconcentration of Fe^{3+} in natural water samples, such as, river water, lagoonwater, springwater, stream water, well water and two water reference materials (NIST-SRM 1640, NIST-SRM 1643d). The obtained preconcentration factor was 82.2, and the detection limit achieved was 5.9 ng ml^{-1}. The recovery of spiked water samples ranged from 95.0 – 103.1%.

The determination of metal ions at low concentration levels usually requires the use of expensive analytical techniques, such as graphite-furnace atomic absorption spectrometry (GFAAS)[1,2] and/or inductively coupled plasma mass spectrometry (ICP-MS).[3,4] Although these techniques present very low detection limits for the determination of several elements in the more difficult kinds of samples, these techniques require a high investment for their implementation and maintenance,[1–4] precluding their extensive application in developing and underdeveloped countries. In order to overcome these difficulties, preconcentration of the elements increases the detection power of less-sensitive analytical techniques, such as flame atomic absorption spectrometry (FAAS) and visible spectrophotometry.

The preconcentration procedure most often employed is solid-phase extraction, because it does not require the use of hazardous solvents, which generate waste to be subsequently treated. Most kinds of the sorbents employed for the preconcentration of the elements in environmental samples are polymeric resins,[5] controlled pore silica glass,[6] modified silica obtained by a grafting process,[7,8] or by the sol-gel method.[9,10] The use of modified silicas with different organic groups is one of the most successful sorbents employed in analytical laboratories, because the silica supports do not swell or shrink such as the polymeric resin;[5] it allows the modified silica sorbent to be used during several cycles of preconcentration, because the retention process (adsorption, chelation, ion exchange) is reversible;[11] the modified silica may be employed in aqueous and organic solvent media;[11] they present good thermal stability[9,10] and appropriated accessibility of the ions to the attached chelanting groups, which allows high preconcentration factors.[11]

In the present work, a new modified silica was synthesized by

reacting 7-amino-4-azaheptyltrimetoxisilane with silica gel, forming 7-amino-4-azaheptyl silica (AAHSG). This sorbent was characterized by infrared spectroscopy, CHN elemental analysis and N_2 adsorption-desorption isoterms; it was successfully employed for the preconcentration of iron(III) in natural water samples. A flow system for the on-line preconcentration of the analyte was employed with spectrophotometric detection at 480 nm.

Experimental

Synthesis and characterization of the 7-amino-4-azaheptyl silica (AAHSG)

The amount of 15 mmol of 1,3-diaminepropane was firstly activated using 15 mmol of sodium hydride in 10 ml of a mixture of aprotic solvent (toluene:tetrahidrofurane) (1:1) for 30 min; then, 15 mmol of 3-chloropropyltrimethoxisilane (CPTMS, ACROS) was added. The mixture was stirred under argon at the solvent-reflux temperature for a period of 5 h. The solution was then centrifuged, to eliminate the by-product sodium chloride. The product of the reaction, 7-amino-4-azaheptyltrimetoxisilane, was then used as an organic precursor reagent for the silica grafting reaction.

Silica gel (Merck) having particle size at 0.02 – 0.05 mm and a surface area of 250 m^2 g^{-1} was activated at 150˚C under a vacuum (10^{-1} Pa) for 5 h. The 7-amino-4-azaheptyltrimetoxisilane was dissolved in 300 ml of toluene and activated silica (10 g) was then added. The mixture was stirred for 48 h under argon at the solvent-reflux temperature. The modified silica was filtered under argon in a Schlenk apparatus, and washed with toluene, hexane, ethyl alcohol, doubly distilled water and ethyl ether (Merck). The resulting sorbent, 7-amino-4-azaheptyl silica (AAHSG), was dried for 2 h under a vacuum at 120˚C.

An infrared analysis was carried out using self-supporting disks of the AAHSG sorbent and pure silica, with an area of 5

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cm², weighing *ca.* 100 mg. The disks were heated for 1 h up to 250˚C, under a vacuum (10^{-2} Torr), using an IR cell, described elsewhere.[9,10] The self-supporting disk was analyzed in the infrared region using a Shimadzu FTIR (Model 8300). Spectra were obtained with a resolution of 4 cm⁻¹, with 100 cumulative scans.

The organic functionalization grade was obtained using a CHN Perkin Elmer M CHNS/O Analyzer (Model 2400). The analysis was performed in triplicate, after heating at 100˚C, under a vacuum, for 1 h.

The nitrogen adsorption-desorption isotherm of degassed solid, at 150˚C, was determined at the liquid-nitrogen boiling point in a homemade volumetric apparatus, with a vacuum line system employing a turbo molecular Edward vacuum pump (Crawley Sussex, England). Pressure measurements were made using a capillary Hg barometer, and also an active Pirani gauge. The specific surface areas of the pure silica and AAHSG sorbent were determined by the BET (Brunauer, Emmett and Teller) multipoint method,[12] and the pore size distribution was obtained using the BJH (Barret, Joyner, and Halenda) method.[13]

Instruments for analytical applications

A 600 S Femto spectrophotometer provided with a 150 μl flow-cell and a serial port RS232C connected to an AMD K6II 350 MHz personal computer for data acquisition were employed throughout for analytical measurements. Two four-channel Milam bp-200 peristaltic pumps provided with Tygon® and silicone tubes of different diameters were used to propel the solutions in the flow system. For pH measurements, a Digimed pH-meter provided with combined glass electrode was used.

Reagents, solutions, samples and reference materials

Doubly distilled water was employed throughout.

Solutions containing 0.1 – 1.0 mol l⁻¹ of hydrochloric acid (Merck) plus 0.5 – 5.0% m/v KSCN were employed as an eluent. A 1.00 g l⁻¹ iron stock solution was prepared from $FeSO_4 \cdot NH_4SO_4 \cdot 6H_2O$. The Fe^{2+} solution was aerially oxidized to Fe^{3+} in an acidic medium. Calibration solutions within 30.0 – 600.0 ng ml⁻¹ (preconcentration) and 2000 – 12000 ng ml⁻¹ (without preconcentration) of Fe^{3+} range were prepared by suitable serial dilution of the stock solution with doubly distilled water and adjusting the final acidity to pH 1.0 with HCl.

For buffer preparations, glacial acetic acid, sodium acetate, ammonium acetate, and sodium hydroxide were employed.

For interference studies, the following salts of the elements were employed: NaCl, KCl, $MgSO_4 \cdot 7H_2O$, $CaSO_4 \cdot 2H_2O$, $AlCl_3 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $Ba(NO_3)_2$, $CrCl_3 \cdot 6H_2O$, Cu metallic dissolved in 10% v/v HNO_3, $MnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$.

Ordinary water samples (river, lagoon, stream, spring, well) were filtered with Whatman paper, and the pH adjusted to 1.0 with HCl; they were then analyzed employing preconcentration procedure.

In order to attain the accuracy of the proposed method, the following water reference materials were employed: Trace Elements in Water NIST-SRM 1643d, and Trace Elements in Natural Water NIST-SRM 1640 from National Institute of Standards and Technology (NIST).

Isotherms of the adsorption of Fe³⁺, Fe²⁺, and Cu²⁺ on AAHSG

A 10.00 ml sample solution containing individually Fe^{3+} or Fe^{2+} (8.95×10^{-6} – 1.79×10^{-2} mol l⁻¹), a Cu^{2+} (7.87×10^{-6} – 1.55×10^{-2} mol l⁻¹) solution plus 10.0 ml of a $NaCH_3CO_2$–HCH_3CO_2 buffer solution (pH 6.0) were transferred to a 50 ml conical polyethylene flask containing 20.0 mg of the sorbent. These

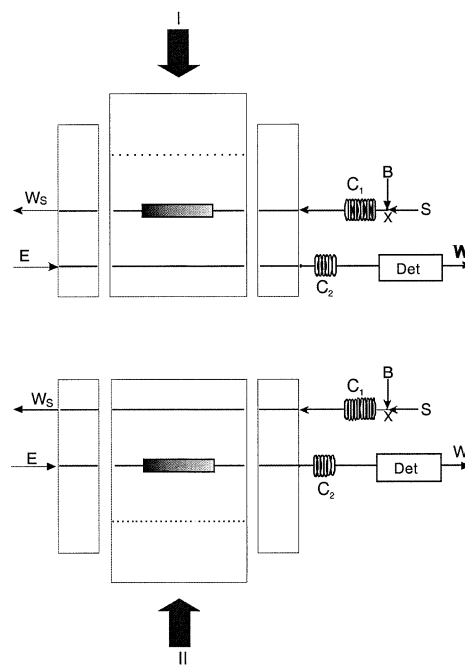Fig. 1   Flow system for the preconcentration of Fe^{3+}. B, Buffer solution (pH 6.2), 2.5 ml min⁻¹; S, sample solution (pH 1), 4.5 ml min⁻¹; C_{R1} and C_{R2}, coil reactors; Ws, waste; E, eluent at 1.2 ml min⁻¹; Det, spectrophotometric flow-cell, 150 μl, $\lambda = 480$ nm.

flasks were placed in a horizontal shaker and agitated for 180 min in order to adsorb the analytes. Subsequently, the solid phase was separated from the aqueous phase by filtration, being the aqueous phase retained for analysis.

The elements, which were not retained in the sorbent, were spectrophotometrically determined. The element Cu^{2+} was determined using 0.15% m/v sodium diethyldithiocarbamate (DDTC); Fe^{3+} was determined using 2.0% m/v KSCN; and Fe^{2+} using 0.25% m/v 1,10-phenantroline. The measurements were carried out using a FEMTO 600 S spectrophotometer, according to the following procedure: an aliquot of 500 μl of the aqueous phase and/or an analyte standard solution plus 1000 μl of acetate buffer (pH 5.0) plus 500 μl of a chromogenic reagent were added to a Hellma glass curvette (10 mm of optical path). The analyte solutions with concentrations higher than those cited above were properly diluted with distilled water. The metal-ion adsorption capacity of the solid phase (N_f), obtained in the saturation plateau was calculated by applying the equation $N_f = (C_s - C_e) \times V/m$, where C_s is the initial metal concentration, C_e is the metal concentration at the equilibrium found in the solution in equilibrium with the solid phase, V is the volume of the solution put with the sorbent, and m is the mass of the solid phase.

Flow system

For the preconcentration of iron in water samples, a manifold made of a Perspex proportional injector-commutator was used, as depicted in Fig. 1. In position I, the sample solution (S, Fe^{3+}) and the buffer solution (B) are merged in the confluence point X; these solutions are subsequently mixed in a coil (C_{R1}) and directed to a glass microcolumn (3 cm, i.d. 3 mm, 0.12 g of sorbent), for sorbing the analyte present in the sample solution, and the aqueous phase is directed to the waste (W_s). In the second line, the eluent solution (E-KSCN + HCl) feeds the
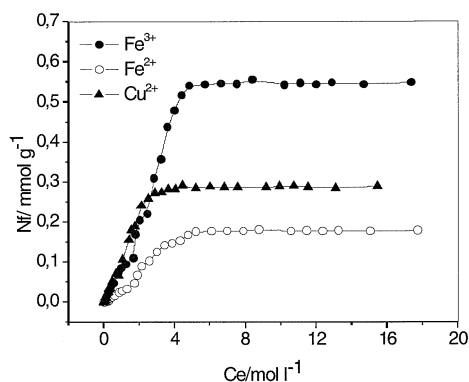
Fig. 2   Adsorption isotherms of Fe^{2+}, Fe^{3+}, and Cu^{2+} on DAPPS. Time of agitation, 180 min.

second coil (C_{R2}), and this solution passes in the flow-cell of the spectrophotometer, producing the line base; subsequently, this solution is directed to the waste (W).   After a 120 s preconcentration period, unless otherwise stated, the central part of the injector commutator is slided to position II, and the microcolumn is inserted in the eluent line, stripping out the retained analyte.   The KSCN present in the eluent solution forms an intense red complex with iron $[Fe(SCN)_x]^{x-3}$, (x ranging 1 – 6),[14] which absorbs at 480 nm.   This solution is mixed in the C_{R2}, and subsequently directed to the spectrophotometer (480 nm), and finally to the waste.   After a suitable elution time (60 s, unless otherwise stated), the central part of the injector-commutator is positioned at position I, and the column is reconditioned with water and a buffer solution. After a period (30 s, unless otherwise stated), the water channel is substituted by the sample solution and a further preconcentration cycle is carried-out.   The total time for a preconcentration cycle and regeneration of the sorbent is 210 s, unless otherwise stated.

Results and Discussion

Synthesis and characterization of the 7-amino-4-azaheptyl anchored silica gel (AAHSG)

The organofunctionalization grade of the AAHSG sorbent obtained by CHN elemental analysis was 0.70 mmol of groups 7-amino-4-azaheptyl per gram of the sorbent.   The presence of the organic groups was also confirmed by infrared spectroscopy.

The specific surface area of the AAHSG sorbent was 230 m^2 g^{-1}, slightly lower than that of pure silica, 250 m^2 g^{-1}, as was expected considering a homogeneous monolayer covering of the surface.   The obtained pore-size distribution curves presented a distribution between 5 and 11 nm in diameter.

Isotherms of the adsorption of Fe^{2+}, Fe^{3+} and Cu^{2+} on AAHSG

The ions Fe^{2+}, Fe^{3+}, and Cu^{2+} were placed into contact with the AAHSG adsorbent for 180 min in order to evaluate the adsorption capacity of this sorbent for these analytes using a batch procedure (Fig. 2).   The maximum adsorption capacity of Fe^{2+}, Fe^{3+} and Cu^{2+} were 0.18, 0.55 and 0.29 mmol g^{-1} (9.1, 31, and 18 mg g^{-1}), respectively.   These results indicate that Fe^{3+} presents a higher affinity by the AAHSG sorbent in relation to Cu^{2+} and Fe^{2+} at pH 6.   Other ions were also tested, and presented a lower affinity by the sorbent at pH 6.   These results

will be shown in the detection concerning to the interference studies.

In this work, no further investigations were carried out with Fe^{2+}, since it is aerially oxidized to Fe^{3+} in water samples, because this kind of sample is usually preserved in 0.1 – 0.2% v/v HNO_3.   Usually, the iron contents are expressed as the total iron concentration form.   For the reasons presented above, Fe^{3+} was chosen for its determination in natural water samples employing an on-line preconcentration system, optimized as described below.

Optimization of the flow system for the preconcentration and figures of merit

The amount of Fe^{3+} that percolates the column is an important variable to be optimized.   The more analyte that percolates the column, the higher is the obtained analytical signal, up to the adsorption capacity of the column, is not surpassed.   It was observed that when 4.5 ml min^{-1} of 400 ng ml^{-1} Fe^{3+} was passed through the column, the highest analytical signal was achieved. For lower sample flow rates, the repeatability of the measurements was worse, but with an increase of the sample flow rate, the %RSD of the measurements (n = 3) was better than 1.5%.   The sample flow rate was fixed at 4.5 ml min^{-1} for improving this work.

It was observed that the maximum signal was obtained when the pH of the buffer solution for the preconcentration was fixed at 6.0 – 6.5.   At lower pH values, there is a competition of the amino groups by protons, since these sites are not available for complex formation.   At pH values higher than 7, Fe^{3+} forms iron hydroxides species, decreasing its sorption on the AAHSG.   In order to obtain the maximum signal, the acidity of the buffer solution was adjusted to pH 6.2 using acetic acid/sodium acetate.

Another variable optimized was the flow rate of the buffer solution; it was observed that the best results were obtained when this variable was set at 2.0 – 2.5 ml min^{-1}.   For lower flow rates, the buffer solution (pH 6.2) was not efficient for mixing with the sample solution (400 ng ml^{-1} Fe^{3+}, pH 1), flowing at 4.5 ml min^{-1}, in order to keep the amino groups of the sorbent non-protonated.   It was also observed that, for flow rates lower than 2.0 ml min^{-1} of the buffer solution, the time to generate the sorbent for a subsequent preconcentration cycle should be increased, while reducing the sample throughput.   For flow rates higher than 2.8 ml min^{-1}, the dispersion was increased, resulting in a decrease of the analytical signal.   As a compromise between the sensitivity and the sample throughput, the flow rate of the buffer solution for the preconcentration of Fe^{3+} was fixed at 2.5 ml min^{-1}.

Other important variable for the preconcentration of elements in the flow system is the composition of the eluent.   In our previous experiments, only HCl was used as an eluent, and KSCN was added in a confluence point, after the column.   In this configuration, the concentration of HCl required for the elution was at least 1.0 mol l^{-1}.   This high acid concentration utilized in the eluent required a regeneration step, using a buffer solution at pH 6.2, for a period of at least 60 s, because the amino groups of the AAHSG were protonated.   This inconvenience leads a diminution of the sample throughput.   In order to overcome these difficulties, a configuration of the flow system, as described in Fig. 1, was employed, where the eluent was formed by a mixture of HCl with KSCN.   This latter component served for stripping out Fe^{3+} from the AAHSG, as well as a chromogenic agent for detecting the analyte.   The effect of the concentration of KSCN presented on the eluent for the preconcentration of Fe^{3+} was also studied.   It was observed

Table 1   Determination of Fe^{3+} in water samples (n = 5) employing an on-line preconcentration system

Sample	$[Fe^{3+}] \pm$ %RSD/ng ml^{-1}		
	Added	Found	Recovery, %
NIST-SRM 1640[a]	0.00	35.6 ± 1.1	—
	30.0	66.7 ± 1.9	103.1
NIST-SRM 1643d[b]	0.00	90.4 ± 1.3	—
	30.0	118.9 ± 2.0	98.3
Countryside river water	0.00	243 ± 1.2	—
	30.0	276 ± 2.1	101.2
Lagoon water	0.00	238 ± 3.0	—
	30.0	275 ± 2.9	102.9
Springwater I	0.00	50 ± 2.0	—
	30.0	79.3 ± 2.4	98.6
Springwater II	0.00	101 ± 2.1	—
	30.0	126 ± 1.7	95.0
Springwater III	0.00	48.8 ± 1.7	—
	30.0	77.8 ± 1.9	98.0
Stream water	0.00	181 ± 1.3	—
	30.0	210 ± 1.7	99.4
Streamlet water	0.00	197 ± 3.3	—
	30.0	220 ± 2.5	96.4
Well water I	0.00	429 ± 1.4	—
	30.0	468 ± 1.1	102.1
Well water II	0.00	228 ± 2.3	—
	30.0	259 ± 1.8	100.4
Well water III	0.00	191 ± 2.4	—
	30.0	219 ± 2.0	99.0

The samples were spiked with 30 ng ml^{-1} Fe^{3+}.
a. Certified value 34.3 ± 5% ng ml^{-1}.
b. Certified value 91.2 ± 4% ng ml^{-1}.

Table 2   Comparison among procedures for Fe^{3+} preconcentration

Sorbent	Characteristics	Ref.
Silica immobilized brow alga	On-line preconcentration, ICP-AES detection; preconcentration factor, 7; DL 11 ng ml^{-1}; total preconcentration time, 2 min	16
Chelex 100-iminodiacetic resin	On-line preconcentration, ICP-AES detection; preconcentration factor, 58.6; total preconcentration time, 2.73 min; DL, 8.4 ng ml^{-1}	17
8-Hydroxy-quinoline immobilized on controlled pore glass	On-line preconcentration, IC-HPLC; postcolumn detection; visible spectrophotometry; DL, 50 mg l^{-1}	18
DAPPS	On-line preconcentration, visible spectrophotometry detection; adsorption capacity, 0.55 mol g^{-1}; preconcentration factor, 82.2; total time of preconcentration, 3.5 min; DL, 5.9 ng ml^{-1}	This work

DL: detection limit.

5.9 ng ml^{-1}.   The quantification limit [10σ/slope analytical curve] was 19.6 ng ml^{-1} (n = 10).

Interference studies

The effect of several elements on the sorption of 400 ng ml^{-1} Fe^{3+} on the AAHSG sorbent (0.12 g) was investigated.   The tolerance level was established at 100 ± 5% as a reference.   Na^{+} and K^{+} ions could be tolerated up to 5000 mg l^{-1}, Ca^{2+} and Mg^{2+} up to 1000 mg l^{-1}, Al^{3+} up to 10 mg l^{-1}, Ba^{2+} up to 20 mg l^{-1}, Co^{2+} up to 10 mg l^{-1}, Cu^{2+} up to 10 mg l^{-1}, Cr^{3+} up to 5 mg l^{-1}, Mn^{2+} up to 10 mg l^{-1}, Ni^{2+} up to 10 mg l^{-1}, Zn^{2+} up to 20 mg l^{-1}. Based on these results, it can be concluded that the method could be successfully applied to the determination of Fe^{3+} in natural water samples, and brackish water, since the concentration of the concomitant species in these kind of samples are usually lower than the proposed preconcentration method can tolerate.[15]

Determination of Fe^{3+} in water samples using the proposed preconcentration system

The proposed preconcentration system using AAHSG as a sorbent was employed for the determination of Fe^{3+} (n = 5) in nine ordinary natural water samples and two reference materials, which were employed for attaining the accuracy of the method (Table 1).   Besides that, a recovery study was also carried out, by spiking the natural water samples with 30 ng ml^{-1} Fe^{3+}.   The recoveries ranged from 95.0 to 103.1%.

Based on the results of Table 1, it can be inferred that Fe^{3+} can be successfully determined in natural water samples, with good accuracy, employing a simple preconcentration system using AAHSG as a sorbent and spectrophotometric detection.

Comparison among several preconcentration methods for iron(III)

In Table 2 are presented some preconcentration procedures for Fe^{3+} determination, employing different sorbents with on-line column preconcentration systems.

As can be seen, the detection limit of this work is slightly lower than the already published on-line preconcentration procedures for iron(III) determination.   This analytical characteristic can be attributed to the higher adsorption capacity (0.55 mmol g^{-1}) of the AAHSG sorbent, which permits higher preconcentration factors with good detection limits, able to determine this analyte in real samples.

that 4.0% m/v KSCN is the best concentration for obtaining higher signals.   The effect of the HCl concentration presented on the eluent for the preconcentration of Fe^{3+} was also studied, since 0.2 mol l^{-1} HCl is sufficient for obtaining the maximum signal.   Based on these results, the best composition of the eluent for the preconcentration was 4.0% KSCN plus 0.2 mol l^{-1} HCl.

The eluent flow rate was also optimized.   It was observed that the best eluent flow rate was 1.0 – 1.2 ml min^{-1}.   For eluent flow rates lower than 1.0 ml min^{-1} the analytical signal was significantly diminished, and the reproductivity of the measurements was compromised.   For eluent flow rates higher than 1.5 ml min^{-1} the analytical signal was also diminished, probably due to dilution of the analyte stripped out from the AAHSG sorbent; it was also observed that the standard deviation of the measurements increased.   For these reasons, the eluent flow rate was fixed at 1.2 ml min^{-1}.

The last variable to be studied was the preconcentrantion time.   The Fe^{3+} preconcentration linearly increased with the time of preconcentration up to 210 s; after that the preconcentration levelled off.   In order to not decrease the sample throughput, the preconcentration time was fixed at 120 s.   In this situation, the sample throughput was 17 measurements per hour.

Using all of the optimized conditions for the preconcentration of Fe^{3+} on the AAHSG sorbent, an analytical curve for the preconcentration was achieved (A = 3.78 × 10^{-3} + 2.27 × 10^{-3}[Fe^{3+}], r = 0.99984, and Fe^{3+} expressed in ng ml^{-1}).   The linearity was obtained for a Fe^{3+} solution ranging from 30 to 600 ng ml^{-1}.   The obtained preconcentration factor was 82.2 and the detection limit, defined as [3σ/slope analytical curve], where σ is the standard deviation of a blank determination n = 20, was

A simple flow preconcentration system for the determination of Fe^{3+} using KSCN as a chromogenic agent and AAHSG as a sorbent was successfully employed for the determination of the analyte in natural and brackish water samples. The AAHSG sorbent used presents a suitable particle size, surface area and porosity, with homogeneous organic chelating groups covering. A preconcentration factor of 82.2 became the proposed method with a detection limit suitable for iron(III) determination in natural water samples.

References

1. E. C. Lima, J. L. Brasil, and A. H. D. P. Santos, *Microchim. Acta*, **2004**, *146*, 22.
2. J. L Brasil, E. C. Lima, R. C. Veses, and M. M. Tisott, *At. Spectrosc.*, **2004**, *25*, 94.
3. N. G. Becka, R. P. Franks, and K. W. Bruland, *Anal. Chim. Acta*, **2002**, *455*, 11.
4. K. Oshita, J. Xu, Y. H. Gao, K. H. Lee, M. Oshima, and S. Motomizu, *Bull. Chem. Soc. Jpn.*, **2003**, *76*, 1555.
5. C. E. Harland, "*Ion Exchange: Theory and Practice*", 2nd ed., **1994**, Royal Society of Chemistry, Cambrige, UK.
6. P. Liu, Q. Pu, and Z. Su, *Anal. Sci.*, **2003**, *19*, 409.
7. S. Zhang, Q. Pu, P. Liu, Q. Sun, and Z. Su, *Anal. Chim. Acta*, **2002**, *452*, 223.
8. M. Zougagh, A. G. Torres, and J. M. Pavón, *Talanta*, **2002**, *56*, 753.
9. J. C. P. Vaghetti, M. Zat, K. R. S. Bentes, L. S. Ferreira, E. V. Benvenutti, and E. C. Lima, *J. Anal. At. Spectrom.*, **2003**, *18*, 376.
10. L. T. Arenas, J. C. P. Vaghetti, C. C. Moro, E. C. Lima, E. V. Benvenutti, and T. M. H. Costa, *Mater. Lett.*, **2004**, *58*, 895.
11. C. Airoldi and R. F. Farias, *Quim. Nova*, **2000**, *23*, 496.
12. S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **1938**, *60*, 309.
13. E. P. Barret, L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **1951**, *73*, 373.
14. A. I. Vogel, "*Química Analítica Qualitativa*", Editora Mestre Jou, **1981**, São Paulo-SP, 274 – 275.
15. Database of Natural Matrix Reference Materials, compilation prepared by International Atomic Energy Agency (IAEA), last update January **2003**, http://www.iaea.org/programmes/nahunet/e4/nmrm/browse.htm, website visited on September 10th, 2004.
16. E. N. V. M. Carillho, J. A. Nóbrega, and T. R. Gilbert, *Talanta*, **2003**, *60*, 1131.
17. C. Pons, M. Miro, E. Becerra, J. M. Estela, and V. Cerda, *Talanta*, **2004**, *62*, 887.
18. M. R. B. Adas, I. A. Takruni, Z. Abdullah, and N. M. Tahir, *Talanta*, **2002**, *58*, 883.