Spectrophotometric determination of thiocyanate by sequential injection analysis

ARTICLE *in* ANALYTICA CHIMICA ACTA · JANUARY 2000

Impact Factor: 4.51 · DOI: 10.1016/S0003-2670(99)00651-0

2 AUTHORS, INCLUDING:

Jacobus (Koos) FREDERICK Van Staden
Institutul National De Cercetare – Dezvoltare …
303 PUBLICATIONS **3,493** CITATIONS

SEE PROFILE

ELSEVIER

Analytica Chimica Acta 403 (2000) 279–286

ANALYTICA CHIMICA ACTA

www.elsevier.com/locate/aca

Spectrophotometric determination of thiocyanate by sequential injection analysis

J.F. van Staden *, A. Botha

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

Received 14 January 1999; received in revised form 2 August 1999; accepted 17 August 1999

Abstract

A sequential injection analysis (SIA) system was developed for the spectrophotometric determination of thiocyanate as $Fe(SCN)^{2+}$. The physical parameters (flow rate, sample and reagent volumes, holding coil and reaction coil internal diameter and length) which influence dispersion in a SIA system were optimized. The effect of the reagent concentration and nitric acid concentration (in the reagent solution and carrier stream, respectively), were also studied. Reagent consumption was effectively reduced by introducing the reagent as a zone into the nitric acid carrier stream, compared to flow injection analysis where the reagent itself is the carrier stream. The system is fully computerized and able to monitor thiocyanate in samples at 24 samples per hour with a relative standard deviation of $<1.20\%$ for samples and standards with thiocyanate concentrations above 10.0 mg l^{-1}. The calibration graph is linear from 2.0 to 150.0 mg l^{-1} with a 3σ detection limit of 1.1 mg l^{-1}. The system has been applied to the determination of thiocyanate in process solutions and waste waters.

Keywords: Thiocyanate; Iron(III); Sequential injection analysis; Process analysis; Waste water samples

1. Introduction

Several methods have been developed for the determination of thiocyanate in waste waters [1–4], biological samples [4–12], metallurgical processes [13] and food [14,15]. A variety of detection systems were applied in these applications for monitoring the level of thiocyanate in samples. The detection systems that were used in these applications include spectrophotometers [1,2,4,7,9,11,13], ion-selective electrodes [3,16], chromatography [5,6,10,15], voltammetry [14], fluorimetry [5], amperometry [8] and flame-atomic absorption spectrometry [12].

The importance of determining thiocyanate levels in effluent streams downstream from a plant outlet can not be underestimated. Though not as toxic as cyanide, thiocyanate is harmful to aquatic life. Thiocyanate is a common constituent of hydrometallurgical solutions [13]. It is formed when pyritic materials are leached with solutions containing cyanide. For efficient plant control it is important continuously to monitor and determine the level of thiocyanate and the subsequent consumption of free cyanide in these process solutions.

The aim of the present study was to develop an automatic procedure for the determination of thiocyanate in process solutions. The existing procedures

* Corresponding author. Tel.: +27-12-420-2515; fax: +27-12-362-5297

E-mail address: koos.vanstanden@chem.up.ac.za (J.F. van Staden)

0003-2670/00/$ – see front matter
PII: S0003-2670(99)00651-0

suffer from low precision [1], high reagent consumption [2,13] and are manually driven [4]. The application of sequential injection analysis (SIA) to the determination of thiocyanate in these process solutions would allow large batches of samples to be determined precisely, continuously, affordably and on-line.

Sequential injection analysis is based on the sequential drawing up of μl of sample and reagent, as zones, into a holding coil. The flow is then reversed and the zones is propelled via a reaction coil to the detector. Mutual penetration of the stacked zones are obtained when the flow is reversed and the result is the formation of a well defined product zone which can be detected spectrophotometrically. The consumption of sample and reagent is dramatically reduced when small volumes are drawn up. This is an advantage over the existing flow injection method in which the reagent acts as the carrier stream [13].

Thiocyanate is determined by its reaction with iron(III) nitrate and spectrophotometric detection of the coloured complex. Thiocyanate reacts with iron(III) to form a series of complexes represented by $[Fe(SCN)_n]^{+3-n}$ where $n = 1$–6. The concentration of thiocyanate determines the number of thiocyanate ions that will coordinate around each iron(III) ion. At relatively low thiocyanate concentrations, the coloured species consists of predominantly $Fe(SCN)^{2+}$ [13]. Thiocyanate can be determined as the $Fe(SCN)^{2+}$, when an excess of iron(III) is present [17].

This reaction has found extensive use in the determination of both iron(III) and thiocyanate. The reaction is fast and, importantly cyanide does not interfere. A disadvantage of this method is the colour instability of the complex. The use of SIA would exclude a delay and measurement of the complex can be conducted before the complex becomes too unstable to deliver reproducible determinations. The optimum conditions were established for the direct determination of thiocyanate by SIA, through the formation of the iron–thiocyanate complex.

2. Experimental

2.1. Reagents and solutions

All reagents were prepared from analytical-reagent grade chemicals unless specified otherwise. All aqueous solutions were prepared using de-ionized water from a Modulab system (Continental Water Systems, San Antonio, TX). The de-ionized water used to prepare the aqueous solutions was degassed by heating to boiling point and cooled.

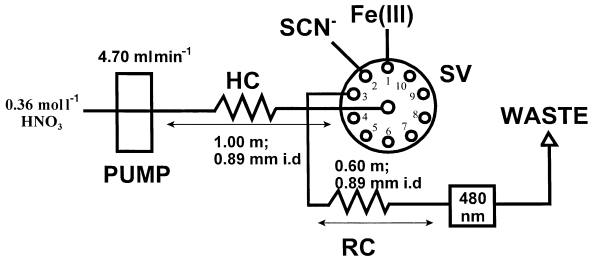

Fig. 1. A schematic diagram of the sequential injection analyser used for the determination of thiocyanate with Fe(III). HC: holding coil, RC: reaction coil, SV: selection valve.

2.1.1. Reagent

The Fe(III) reagent solution was prepared by dissolving 3.5 g of $Fe(NO_3)_3 \cdot 9H_2O$ in ca. 25 ml of water. A 10 ml volume of 65% (m/m) HNO_3 was added to the iron solution after which it was diluted to 100 ml with water.

2.1.2. Thiocyanate solution

A 1000 mg l^{-1} thiocyanate stock solution was prepared by dissolving 0.1311 g of NH_4SCN in ca.25 ml of water and diluting the resulting solution to 100 ml. This solution was standardized by the Volhard method. A 50 mg l^{-1} thiocyanate working solution was prepared by appropriate dilution of the stock solution.

2.1.3. Carrier solution

A 0.36 mol l^{-1} HNO_3 carrier was prepared by diluting 50 ml of 65% (m/m) HNO_3 to 2.0 l.

2.2. Apparatus

The sequential injection system schematically outlined in Fig. 1 was constructed from the following components: a Gilson Minipuls peristaltic pump (Model M312, Villiers-le-Bel, France); a 10-port electrically actuated selection valve (Model ECSD10P; Valco Instruments, Houston, TX); and a Unicam 8625 UV–Visible spectrophotometer equipped

with a 10 mm Hellma (Mülheim/Baden, Germany) flow-through cell (volume 80 μl) for absorbance measurements.

Data acquisition and device control was achieved using a PC30-B interface board (Eagle Electric, Cape Town, South Africa) and an assembled distribution board (Mintek, Randburg, South Africa). The FLOWTEK [18] software package (obtainable from Mintek) for computer-aided flow analysis was used throughout for device control and data acquisition. All the data given (relative peak heights) are the mean for $n = 10$.

The wavelength of maximum absorbance was identified by scanning the $Fe(SCN)^{2+}$ complex solution over the 300–800 nm range with a Spectronic Genesys 5 spectrophotometer (Milton Roy Company). The optimum wavelength was chosen as 480 nm which corresponds to the wavelength used by previous authors conducting the same determination [13].

To compare the results from the proposed SIA system, the thiocyanate concentrations of various process solutions and waste water samples, containing different trace or minor amounts of cyanide and metal cyanide complexes, were also determined manually with a Hewlett-Packard 8453 diode array spectrometer (Germany).

2.3. Procedure

The device sequence for the determination of thiocyanate by SIA is given in Table 1.

3. Results and discussion

3.1. Optimization

All the data given (relative peak heights) in the optimization of the physical and chemical parameters are the mean values and the % relative standard deviation (RSD) obtained, calculated for $n = 10$.

3.1.1. Physical parameters

The physical parameters of a SIA system affect the degree of dispersion and the zone penetration obtained when the reagent and sample zones are propelled to the detector along the flow conduit. It is important to optimize these parameters to obtain optimum mixing of the zones and deliver an appreciable amount of the detectable species.

3.1.1.1. Flow rate. The reaction between iron(III) and thiocyanate is fast, resulting in the immediate formation of $Fe(SCN)^{2+}$. At high flow rates the time available for complex formation is much less than at lower flow rates, So that an inadequate amount of $Fe(SCN)^{2+}$ is formed for spectrophotometric detection at the high flow rates, resulting in decrease in sensitivity at higher flow rates (Fig. 2). Greatest sensitivity was obtained for flow rates between 3.0 and 5.0 ml min^{-1}. The optimum flow rate was chosen as 4.7 ml min^{-1}.

3.1.1.2. Reagent and sample volumes. The sample volume was optimized by varying it for three fixed reagent volumes. The effect of sample volume on the linear range of thiocyanate was studied. The aim was to obtain optimum sensitivity for small thiocyanate concentrations including the widest linear range possible. The results are summarized in Table 2. For each fixed reagent volume, the sensitivity increased and the linear range decreased for the larger sample volumes. The decrease in linear range was due to the absorbance becoming too high for the spectrophotometer to measure.

The results obtained for the different fixed reagent volumes can be compared by choosing identical reagent : sample volume ratios. For a 2 : 1 ratio, an increase in sensitivity was observed when increasing the reagent volume from 100 to 140 μl, after which the sensitivity stabilized for a reagent volume of 200 μl. For larger volume ratios much more reagent and sample was available to react, thus an increase in complex formation was obtained. A disadvantage of the larger volume ratios and the larger reagent volumes is that it increases the analysis time due to the time that is necessary to draw up the solutions and rinse the system. This effectively decreases the sampling frequency. The larger volume ratios also decrease the linear range.

An optimum sample volume was chosen by considering the results which were obtained for a fixed reagent volume of 140 μl. A fixed reagent volume of

Table 1
Device sequence for one cycle of the sequential injection system

Time (s)	Pump	Valve	Description
0	Off	$Fe(NO_3)_3{\cdot}9H_2O$	Pump off, select $Fe(NO_3)_3{\cdot}9H_2O$ stream (valve position 1)
5.0	Reverse		Draw up $Fe(NO_3)_3{\cdot}9H_2O$ solution
6.8	Off		Pump stop
7.8		NH_4SCN	Select NH_4SCN stream (valve position 2)
8.8	Reverse		Draw up NH_4SCN solution
9.7	Off		Pump stop
10.7		Detector	Select detector line (valve position 3)
11.7	Forward		Pump stack of zones to detector
150	Off	Home	Pump off, return valve to starting position (valve position 1)

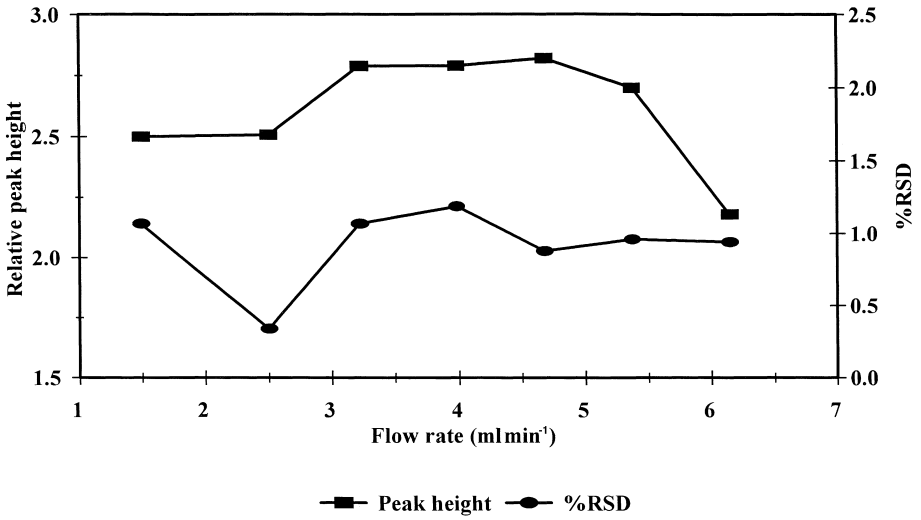

Fig. 2. Influence of flow rate on sensitivity and precision.

Table 2
Optimization of the sample volume for three fixed reagent volumes

Volume (reagent) (μl)	Volume (sample) (μl)	Relative peak height $[SCN^-]$ ($mg\,l^{-1}$)			
		10	50	100	200
100	50	0.41	1.72	3.25	5.51
	100	0.51	2.43	4.41	7.4
	200	0.82	3.52	6.34	–
140	70	0.61	2.62	4.86	8.17
	140	0.82	3.95	6.83	–
	280	1.25	5.42	–	–
200	50	0.54	2.56	4.62	8.05
	100	0.84	3.74	6.72	–
	200	1.16	4.95	8.57	–
	400	1.7	6.74	–	–

Table 3
Optimization of the reagent volume for a sample volume of 70 μl

Volume (reagent) (μl)	Relative peak height [SCN^-] ($mg\,l^{-1}$)			
	10	50	100	200
140	0.66	2.75	5.27	8.35
210	0.82	3.4	5.97	–
280	0.63	3.28	5.95	–

140 μl gave the best results regarding high sample frequency and wide linear range with good sensitivity for smaller thiocyanate concentrations, compared to the other fixed reagent volumes which were studied. The optimum sample volume was chosen as 70 μl.

The reagent volume was optimized for a sample volume of 70 μl. The results are shown in Table 3. For reagent volumes smaller than 140 μl no response was obtained due to inadequate overlapping of the zones. For the larger reagent volumes an increase in sensitivity was obtained as was a decrease in linear range. A reagent volume of 140 μl was chosen as optimum as it gave a good response for the smaller thiocyanate concentrations as well as a wide linear range.

3.1.1.3. Holding coil. The holding coil (HC) dimensions, internal diameter (i.d.) and length, affect the dispersion of the sample and reagent zones when it is drawn up into it [19]. The effect of internal diameter (i.d.) on sensitivity and reproducibility was studied by keeping the volume of the holding coil constant and changing the i.d. The results are depicted in Table 4. The effect of i.d. on sensitivity is negligible since there is not much change in peak height for different i.d. values. The reproducibility decreased for the larger i.d. values with 0.76 mm giving the best results. The optimum i.d. was chosen as 0.89 mm since a lot of back pressure was experienced in the flow conduit for the 0.76 mm i.d..

The effect of HC length on sensitivity and precision was studied at the optimum HC i.d of 0.89 mm. A decrease in sensitivity was observed for the longer coils. The best sensitivity and reproducibility was obtained for a HC length of 1.0 m.

3.1.1.4. Reaction coil. The reaction coil (RC) has a more pronounced effect on the reagent and sample zone dispersion than the HC. The zones are propelled via the reaction coil to the detector and the RC dimensions must be chosen in order to minimize dispersion of the product zone formed and to deliver optimum sensitivity.

The i.d.of the RC was studied by keeping its volume constant and changing the i.d. The results are given in Table 5. A decrease in sensitivity was observed for the larger i.d. values due to the frictional effect of the tubing walls. This effect decreases with increase in i.d. with the result that axial dispersion is reduced [20]. This contributes to the decrease in sensitivity. An i.d. of 0.89 mm was chosen as optimum because good sensitivity and the best reproducibility.

The length of the RC determines the amount of dispersion that the zones will undergo on the way to the detector. Table 5 depicts the change in sensitivity for different RC lengths studied at an optimum RC i.d. of 0.89 mm. The longer the length of the RC, the higher will be the dispersion of the zones. This is confirmed by the results as a decrease in sensitivity was obtained for the longer RC lengths due to increased dispersion. A RC length of 0.6 m gave good sensitivity and the best reproducibility and was chosen as the optimum.

3.1.2. Chemical parameters

3.1.2.1. Reagent concentration ($Fe(NO_3)_3{\cdot}9H_2O$). The reagent concentration was optimized by studying its effect on the thiocyanate linear range. An increase in sensitivity was observed for increased reagent concentrations (Table 6). The increase in sensitivity was more pronounced for the higher thiocyanate concentrations due to the excess of sample that was available to react with the reagent compared to the limited amount of sample available at the lower thiocyanate concentrations.

A decrease in the thiocyanate linear range was also observed for the higher reagent concentrations. A $35\,g\,l^{-1}$ reagent concentration, which gave the widest thiocyanate linear range and the best sensitivity for this linear range, was chosen as optimum.

3.1.2.2. Nitric acid concentration. The effect of the nitric acid concentration was studied by changing its

Table 4
Effect of holding coil internal diameter (i.d.) and length on sensitivity and reproducibility

i.d. (mm)	Relative peak height	RSD (%)	Length[a] (m)	Relative peak height	RSD (%)
0.76	2.99	0.3	0.75	3.15	1.08
0.89	3.07	1.37	1	3.18	0.51
1.14	2.99	1.55	1.25	3.1	0.72
1.6	2.97	1.53	1.5	3.01	1.39

[a] Constant i.d. of 0.89 mm.

Table 5
Effect of reaction coil internal diameter (i.d.) and length on sensitivity and reproducibility

i.d. (mm)	Relative peak height	RSD (%)	Length[a] (m)	Relative peak height	RSD (%)
0.64	3.02	0.95	0.4	2.94	0.91
0.76	3.05	0.76	0.5	3.11	1.02
0.89	2.98	0.34	0.6	2.93	0.84
1.14	2.72	1.26	0.8	2.64	1.12
			1.0	2.67	1.26

[a] Constant i.d. of 0.89 mm.

Table 6
The effect of the reagent ($Fe(NO_3)_3{\cdot}9H_2O$) concentration on the thiocyanate linear range

Reagent ($g\,l^{-1}$)	Relative peak height [SCN^-] ($mg\,l^{-1}$)				
	10	50	100	150	200
10	0.32	1.71	3.2	4.55	5.91
20	0.50	2.34	4.41	6.31	7.50
35	0.59	2.90	5.16	7.30	9.28
50	0.63	2.89	5.49	7.94	–
75	0.61	3.16	5.86	8.66	–

Table 7
Effect of nitric acid concentration, in the reagent solution and carrier stream on sensitivity

[HNO_3] in reagent solution ($mol\,l^{-1}$)	Relative peak height [HNO_3] in carrier stream ($mol\,l^{-1}$)			
	0.36	1.44	2.88	5.76
0.36	2.77	2.34	1.95	1.36
1.44	2.76	2.45	2.19	1.75
2.88	2.75	2.46	2.29	1.95
5.76	2.75	2.66	2.43	2.17

concentration in the reagent solution and the carrier stream. Four acid concentrations were studied: 0.36, 1.44, 2.88 and 5.76 $mol\,l^{-1}$. For each of the four carrier stream acid concentrations, four reagent solutions with the four different acid concentrations mentioned were studied. In total, 16 different combinations were studied. The results are summarized in Table 7. For each respective reagent solution a decrease in sensitivity was observed for higher carrier stream concentrations. When keeping the carrier stream concentration constant, an increase in sensitivity was observed for the higher reagent solution acid concentrations. This increase was more pronounced for the higher carrier stream concentrations and negligible for the small carrier stream concentrations.

A 0.36 $mol\,l^{-1}$ carrier stream nitric acid concentration gave the best sensitivity for the iron(III)–thiocyanate reaction. This concentration is also the best choice when considering the physical aspects of the flow conduit. High acid concentrations can attack the Tygon tubing thus reducing its life span.

Since the differences in sensitivity between the reagent solutions were negligible for a 0.36 $mol\,l^{-1}$ carrier stream nitric acid concentration, it did not really matter which acid concentration was decided upon. A 1.44 $mol\,l^{-1}$ reagent acid concentration was chosen as optimum. If the acid concentration is too low, reduction of iron(III) can not be prevented effectively, and a too high acid concentration can reduce the rate of complex formation.

4. Method evaluation

The proposed SIA system was critically evaluated with regard to accuracy, precision, detection limit, linear range, sample interaction, sampling frequency and interferences.

Table 8
Comparison of results obtained by the proposed SIA system and diode array spectrophotometry

Samples	Diode array ($mg\,l^{-1}$)	SIA ($mg\,l^{-1}$)	RSD (%) (SIA)
A[a]	133	130	0.38
B[a]	89	95	0.35
C[a]	117	122	0.49
D[b]	29	30	0.8
E[a]	107	108	0.45
F[a]	68	70	0.71
G[b]	6.4	6.9	3.30

[a] Process solutions.
[b] Waste water samples from effluent streams.

Table 9
Interference from foreign ion species studied with $8.61 \times 10^{-4}\,mol\,l^{-1}$ ($50.0\,mg\,l^{-1}$) thiocyanate[a]

Tolerance ratio (by wt.) of foreign species (x)	Foreign species
1000	Ni^{2+}; SO_4^{2-}
700	Zn^{2+}
300	Mn^{2+}; $C_2O_4^{2-}$
50	Cu^{2+}
30	F^-
0.66	$Fe(CN)_6^{3-}$
0.44	$Fe(CN)_6^{4-}$

[a] The ratio of foreign ion to thiocyanate is indicated as $x:1$. The mole ratio is indicated.

4.1. Linearity, accuracy, precision and detection limit

The response of the proposed SIA system for the spectrophotometric determination of thiocyanate was evaluated under optimum conditions. The calibration graph was linear from 2.0 to $150.0\,mg\,l^{-1}$ (peak height absorbance = $0.04934[SCN^-] + 0.02138$; $r = 0.9996$, $n = 10$).

The detection limit gives an indication of the lowest thiocyanate concentration that can be distinguished from the background signal with 99% certainty. The detection limit is calculated by using the following formula:

$$\text{Detection limit} = \frac{(3\,S_b + I_b) - k}{m}$$

where S_b is the standard deviation of the background signal; I_b represents the relative peak height of the background signal; k is the intercept of the calibration graph; m is slope of the calibration graph.

The calculated detection limit was $1.1\,mg\,l^{-1}$ SCN^-.

The accuracy of the proposed system was evaluated by analyzing seven process solutions and waste water samples from the process effluent streams. The results, shown in Table 8, are in good agreement with the results obtained with the diode-array spectrophotometer using the thiocyanate procedure. The precision determined for the analyzed samples ($n = 10$) is also shown in Table 8. In all cases the RSD was $<0.90\%$, except for thiocyanate concentrations below $10.0\,mg\,l^{-1}$.

A sampling frequency of 24 samples per hour was obtained. The interaction between samples was $<0.80\%$, which is negligible.

4.2. Interferences

The practicality of a procedure is evaluated by its ability to function in the presence of interferences. A few species are known to interfere in the determination of thiocyanate by the iron(III) procedure. An important feature of this method is the non-interference of cyanide. This makes the proposed SIA procedure ideally suited for application in hydrometallurgical solutions. $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ were tested as possible interferences, because they are present in hydrometallurgical solutions [13]. Fluoride, sulfate and oxalate, which form complexes with iron(III) in acidic solutions, were also tested though they are not commonly found in process solutions. The results of the interference study are highlighted in Table 9. Interference from $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ at mole ratios of 0.44 and 0.66 to thiocyanate (these ratios correspond to 80.0 and $120.0\,mg\,l^{-1}$, respectively), are acceptable since the concentrations of these metal complexes are generally below a mole ratio of 0.55 ($100.0\,mg\,l^{-1}$), but depend on the composition of the hydrometallurgical solutions [13]. The large interference of fluoride is ascribed to the strong complex formation with iron(III) and that of copper(II) to complex formation with thiocyanate. Interferences from nickel(II), sulfate, zinc(II), manganese(II) and oxalate are negligible at the levels that were studied.

5. Conclusions

Sequential injection analysis was successfully applied to the determination of thiocyanate in process so-

lutions and waste water samples. The simplicity of the manifold makes it ideally suited for use as an on-line analyser for the monitoring of thiocyanate in process streams, effluent solutions and hence the control of environmental pollution. The system is robust, simple to operate and capable of rapid automatic analysis when computer controlled. The calibration graph is linear from 2.0 to 150.0 mg l^{-1} with a detection limit of 1.1 mg l^{-1}. The system processes 24 samples per hour with a relative standard deviation of $<1.20\%$ for samples and standards with thiocyanate concentrations above 10.0 mg l^{-1}.

References

[1] A. Mohammad, J.P.S. Chahar, J. Chromatogr. A 774 (1997) 373.
[2] A.A. Ensafi, Indian J. Chem. Sect. A 36A (1997) 344.
[3] V. Trajkovska, K. Kaladzievski, Anal. Lab. 5 (1996) 266.
[4] A.A. Ensafi, J. Tajebakhsh-E-Ardakany, Anal. Lett. 28 (1995) 731.
[5] S.H. Chen, Z.Y. Yang, H.L. Wu, H.S. Kou, S.J. Lin, J. Anal. Toxicol. 20 (1996) 38.
[6] C. Bjergegaard, P. Moller, H. Sorensen, J. Chromatogr. A. 717 (1995) 409.
[7] P. Lundquist, B. Kagedal, L. Nilsson, Eur. J. Clin. Chem. Clin. Biochem. 33 (1995) 343.
[8] E.G. Cookeas, C.E. Efstathiou, Analyst (London) 119 (1994) 1607.
[9] G.Z. Zhang, S.J. Liu, X.W. He, H.M. Shi, Fenxi Huaxue 21 (1993) 905.
[10] Y. Michigami, K. Fujii, K. Ueda, Y. Yamamoto, Analyst (London) 117 (1992) 1855.
[11] F. Olea, P. Parras, J. Anal. Toxicol. 16 (1992) 258.
[12] D. Chakraborty, A.K. Das, Indian J. Technol. 26 (1988) 350.
[13] E.A. Jones, M.J. Hemmings, S. Afr. J. Chem. 42 (1989) 6.
[14] Y. Liu, J.Y. Wang, Y.Y. Wang, Fenxi Huaxue 24 (1996) 985.
[15] Z.M. Fu, S.H. Ni, Z.H. Pang, Fenxi Shiyanshi 12 (1993) 85.
[16] L.G. Evsevleeva, Yu.I. Urusov, O.M. Petrukhin, Yu.A. Borzhitski, Zh. Anal. Khim. 47 (1992) 608.
[17] Z. Marczenko, Spectrophotometric Determination of Elements, Ellis Horwood, Chichester, 1976.
[18] G.D. Marshall, J.F. van Staden, Anal. Instrumentation 20 (1992) 79.
[19] J.F. van Staden, A. Botha, S. Afr. J. Chem. 51 (1998) 100.
[20] G.D. Marshall, J.F. van Staden, Process Control and Quality 3 (1992) 251.