Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1051 (2004) 303–308
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of volatile corrosion inhibitors by capillary electrophoresis

Elisabete A. Pereira*, Marina F. M. Tavares

Institute of Chemistry, University of São Paulo, P.O. Box 26077, 05513-970 São Paulo, SP, Brazil

Abstract

In this work, a capillary electrophoresis (CE) method using indirect UV detection (214 nm) for the simultaneous determination of monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diethylethanolamine (DEEA), monocyclohexylamine (MCHA) and dicyclohexylamine (DCHA) in water/ethanol extracts of wrapping materials containing volatile corrosion inhibitors (VCIs) was described. A running buffer consisting of 0.010 mol L^{-1} imidazole, 0.010 mol L^{-1} 2-hydroxyisobutyric acid (HIBA) and 0.010 mol L^{-1} 18-crown-6 ether enabled separation of the analytes in less than 7 min. A few method validation parameters were determined revealing good migration time repeatability (<0.7% RSD) and area repeatability (<1.8% RSD). Limits of detection were in the range of 0.52–1.54 mg L^{-1}. Recovery values were in the range of 94.8–100.9%. The methodology was successfully applied to the analysis of three commercial products (VCI treated paper, foam and plastic). The concentration of amines in these materials varied from 0.050 to 22.3% (w/w).

Keywords: Volatile corrosion inhibitors; Capillary electrophoresis; Amines; Cations

1. Introduction

Corrosion is a naturally occurring phenomenon, commonly defined as the deterioration of a substance, usually metals or their properties, due to environmental impact [1–3]. It is well accepted that the corrosion process occurs more rapidly in the presence of trace amounts of atmospheric pollutants such as SO_2, NO_2, Cl^- and F^- and it is enhanced by a combination of high humidity (greater than 70%) and high temperature [1].

The conventional approach to protect metal surfaces from corrosion especially during transport and storage involves the selection of corrosion-resistant alloys or the use of protective coatings or paints [1,4]. These preventive measures are often costly and not practical. An effective and relatively inexpensive means of controlling corrosion in closed environments is the use of volatile corrosion inhibitors (VCIs) [5].

Considering that the corrosion efficiency varies according to the amount and type of chemical product used in the VCI formulation, determining their chemical composition is critical not only for better understanding of their role in the corrosion process, but also for the developing of new formulations.

Gas chromatography (GC) [6–9] and high-performance liquid chromatography (HPLC) [10–24] are the most widely adopted techniques for the measurement of aliphatic and cyclic amines in various matrices. However, these methods have presented some practical limitations. Direct gas chromatographic analysis of aliphatic amines requires packed columns or capillary columns coated with thick films of special material [8]. In conventional HPLC, aliphatic amines are more difficult to be determined because they are poorly retained on C_{18} reversed-phase columns at the pH values commonly used and do not absorb strongly in the UV–vis region [12]. Alternatively, ion-exchange chromatography (IC) has been used [23,24] but this mode leads to long separation times and in IC, the choice of mobile phase is somehow restricted due to swelling of the polymeric support.

Capillary electrophoresis (CE) represents an attractive alternative for the determination of non-chromophoric amines.

* Corresponding author. Present address: Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508-900 São Paulo, SP, Brazil.
E-mail address: ealves@iq.usp.br (E.A. Pereira).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.08.044

In CE, amines are generally separated as cationic species, and detected indirectly using low-pH electrolyte systems containing UV-absorbing additives [25–29]. In this work, the development of a rapid analytical method to analyze volatile corrosion inhibitors in wrapping materials by capillary electrophoresis is described. The applicability of the proposed method is demonstrated by the analysis of three commercial products (VCI treated plastic, foam and paper materials).

2. Experimental

2.1. Instrumentation

All experiments were conducted in a capillary electrophoresis system (Agilent Technologies, model HP 3D CE, Palo Alto, CA, USA), equipped with a diode array detector set at 400 nm (reference at 214 nm) for indirect detection and a temperature control device maintained at 29 °C. Data acquisition and treatment software was supplied by the manufacturer (HP ChemStation, rev A.06.01). Fused-silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) with dimensions 53.5 cm total length, 45 cm effective length and 75 μm i.d. × 375 μm o.d. were used. Samples were injected hydrodynamically, 50 mbar pressure (1 mbar = 100 Pa) during 3 s. The electrophoresis system was operated under normal polarity and constant voltage conditions of +18 kV.

2.2. Reagents and solutions

All reagents and solvents were of analytical grade and used with no further purification. Monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diethylethanolamine (DEEA) and monocyclohexylamine (MCHA) were obtained from Aldrich (Milwaukee, WI, USA). Dicyclohexylamine (DCHA) was obtained from Merck (Darmstadt, Germany). Stock solutions at 1000 mg L^{-1} concentration were prepared by dissolving appropriate amounts of the selected standards in deionized water (Milli-Q, Millipore, Bedford, MA, USA). The optimal electrolyte solution comprised 0.010 mol L^{-1} imidazole, 0.010 mol L^{-1} hydroxyisobutyric acid (HIBA) and 0.010 mol L^{-1} 18-crown-6 ether.

2.3. Analytical procedure

The electrolyte solution was prepared fresh daily. At the beginning of each day, the fused-silica capillary was conditioned by flushing with a 1 mol L^{-1} NaOH solution (5 min), followed by a 5 min flush of deionized water and electrolyte solution (40 min). In between runs, the capillary was just replenished with fresh electrolyte solution (3 min flush). Specific electrophoretic conditions and separation electrolytes are stated in the figure legends.

2.4. Sample extraction

VCI treated samples of wrapping materials (plastic, paper and foam) were obtained from a local manufacturer (VCI Brasil, Bauru, SP, Brazil). Two extraction procedures were studied using a VCI plastic sample (FBL VCI 69180 mic 4 mm × 1000 mm) as reference material.

2.4.1. Procedure A

This procedure involved the dissolution of 0.5 g of the commercial plastic sample in 5.0 mL toluene at 100 °C. After complete dissolution, the polymer was precipitated by the addition of 10 mL methanol followed by filtration. The toluene phase was separated by addition of 10 mL deionized water. The methanolic layer was transferred into a 25 mL volumetric flask and the volume was completed with deionized water. The solution was filtered in a 0.45 μm membrane and analyzed by CE.

2.4.2. Procedure B

The extraction method was performed using 0.5 g of the commercial plastic sample and 25 mL of 90:10 (v/v) water:ethanol. The mixture was vigorously stirred and placed in an ultrasonic bath for 20 min. The resulting solution was filtered in a 0.45 μm membrane and analyzed by CE. This procedure was further employed in the analysis of VCI treated foam and paper samples.

3. Results and discussion

3.1. Optimization of the separation conditions

The most important optimization step in the separation of non-absorbing cationic compounds is the choice of a suitable background electrolyte co-ion because of peak symmetry considerations and the population of system peaks. The use of protonated imidazole as UV co-ion for the separation of aliphatic amines and inorganic cations was first reported by Beck and Engelhardt in 1992 [25] and since then it became a popular choice. Several other cationic chromophores have been reported in the literature with adequate performance. When the separation selectivity needs to be improved a variety of electrolyte additives from small organic acids (HIBA, lactate, etc.) to inclusion complexing agents (crown ether) can be selected [26–30].

In this work, several electrolyte systems and instrumental parameters were studied to achieve the best resolution, highest sensitivity and shortest analysis time for the analysis of the selected amines. Electrolyte systems comprising of imidazole, HIBA and 18-crown-6 ether performed best and they were chosen for further optimization.

The effect of imidazole concentration on separation was first studied in the range of 0.005–0.015 mol L^{-1}, with constant additives concentration, pH and applied voltage (0.005 mol L^{-1} 18-crown-6 ether, 0.010 mol L^{-1} HIBA, pH

4.3, +20 kV, fused-silica capillary 48.5 cm total length, 40 cm effective length, and 75 μm i.d. versus 375 μm o.d.). With increasing imidazole concentration it was observed a gain in analytical signal and a decrease in baseline noise. However higher-concentration buffers are more conductive, draw higher currents, and generate more Joule heating than more dilute solutions. Therefore, a imidazole concentration of 0.010 mol L^{-1} was selected because it represented a compromise among analytical signal, current counts and analysis time.

Even though HIBA has been used in the context of cation separations as a complexing agent, in this work HIBA (pK_a = 3.97) was used simply for buffering the electrolyte. Buffered electrolytes tend to be used in CE to limit the possible variations caused by changes in pH and to deliver results with better reproducibility.

Finally, addition of a complexing agent (18-crown-6 ether) to the electrolyte was necessary for the complete resolution of the amines under evaluation. In acidic conditions, amines are fully protonated and are known to form complexes with crown ethers. The increase of 18-crown-6 ether concentration (0.005–0.010 mol L^{-1}) resulted in an improvement in the separation of DEA and MCHA, however, concentrations above 0.010 mol L^{-1} had a negligible effect on the separation. Therefore in this study, 0.010 mol L^{-1} 18-crown-6 ether was chosen as the optimum concentration. Fig. 1A presents the separation of the amine standards in an imidazole electrolyte buffered with HIBA. The effect of crown ether in the separation is shown in Fig. 1B and its increase in Fig. 2 and the effect of increased concentration of imidazole is shown in Fig. 1C.

The influence of the applied potential and column length on the separation the amines were next evaluated using an electrolyte system containing 0.010 mol L^{-1} imidazole, 0.010 mol L^{-1} HIBA and 0.010 mol L^{-1} 18-crown-6 ether, pH 4.3. As expected, at a higher potential (25 kV) the analysis time was reduced, however losses of resolution were observed between DEA, MCHA and DEEA (not shown). By increasing capillary length, resolution was improved (not shown). Optimum separation, that it represents a compromise among analysis time and resolution, was obtained at 18 kV using a fused-silica capillary with dimensions 53.5 cm total length, 45 cm effective length and 75 μm i.d. by 375 μm o.d. The separation of the six amines under investigation at the optimized conditions is shown in Fig. 2.

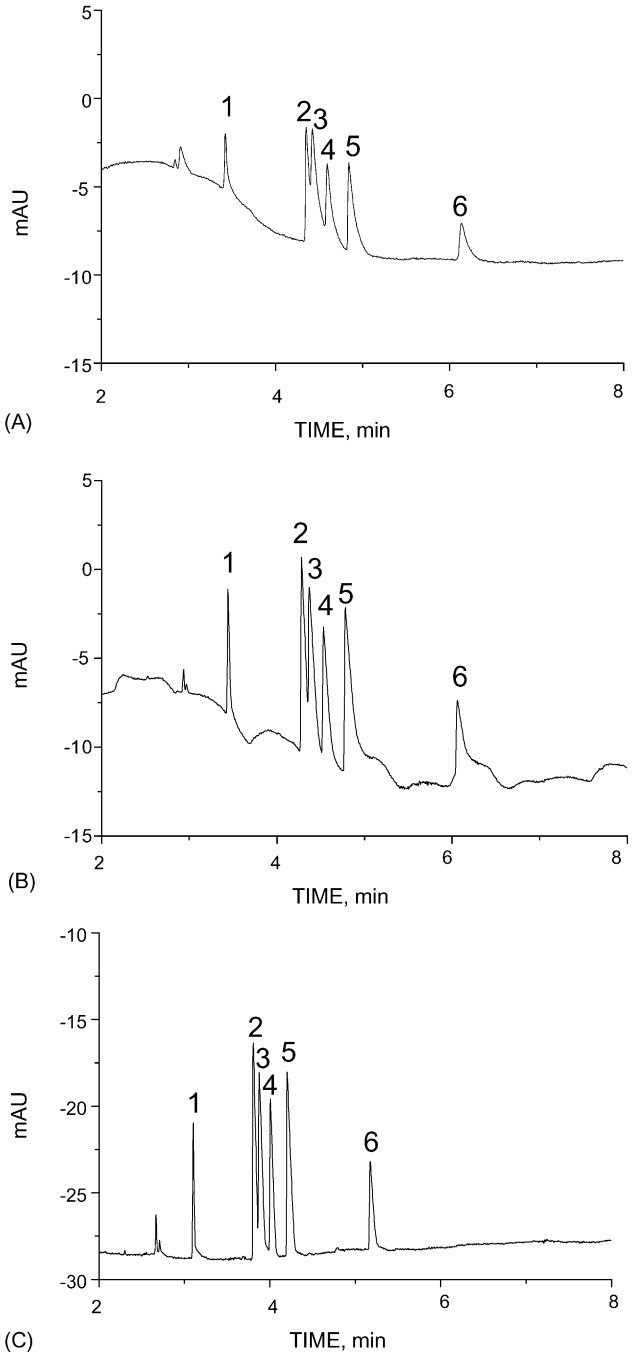

Fig. 1. Optimization of the electrolyte composition. Separation conditions: fused-silica capillary, 75 μm i.d. 360 μm × o.d., 48.5 cm total length (40 cm to detector); separation voltage: 20 kV; hydrodynamic injection: 3 s at 50 mbar; (A) 0.010 mol L^{-1} imidazole, 0.010 mol L^{-1} HIBA, pH 4.3; (B) 0.010 mol L^{-1} imidazole, 0.010 mol L^{-1} HIBA and 0.005 mol L^{-1} 18-crown-6 ether, pH 4.3; (C) 0.015 mol L^{-1} imidazole, 0.010 mol L^{-1} HIBA and 0.005 mol L^{-1} 18-crown-6 ether, pH 4.3. Peak identification: 1, MEA; 2, DEA; 3, MCHA; 4, DEEA; 5, TEA; 6, DCHA.

3.2. Optimization of the extraction procedure

A VCI treated plastic sample was spiked with known quantities of MEA, DEA, TEA, DEEA, MCHA and DCHA and subsequently submitted to the extraction procedures described in Section 2. Extraction efficiencies were evaluated by comparing the experimentally determined amine concentration in the spiked samples with nominal values. Acceptable recoveries were obtained when procedure B was employed as shown by the data compiled in Table 1. Procedure B uses an ethanolic solution at room temperature as extraction medium. Before assessing the VCI contents of real samples further optimization of the extraction conditions in procedure B was attempted.

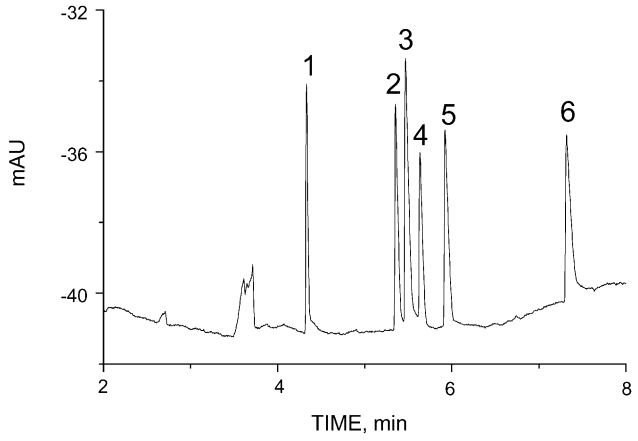

Fig. 2. Optimized separation of the amines under investigation. Concentration of each amine standard: 10 mg L^{-1}. Separation conditions: fused-silica capillary, 75 μm i.d. × 360 μm o.d., 53.5 cm total length (45 cm to detector); separation voltage: 18 kV; hydrodynamic injection: 3 s at 50 mbar; separation electrolyte: 0.010 mol L^{-1} imidazole, 0.010 mol L^{-1} HIBA and 0.010 mol L^{-1} 18-crown-6 ether, pH 4.3; indirect UV-absorbance detection at 214 nm; temperature 29 °C. Peak labels as in Fig. 1.

Representative amounts of a VCI treated plastic sample, containing DCHA in its formulation, were weighted and subsequently extracted with water/ethanol mixtures of different ratios. Increasing the ethanol phase in the range of 10–50% no significant changes in the extraction efficiency were observed. Therefore a fixed amount of ethanol (10%) was chosen for further studies.

New pieces of the VCI treated plastic sample were then spiked with a mixture of the amine standards and subsequently extracted with 25 mL of a 90:10 (v/v) water:ethanol solution. The mixture was vigorously stirred and placed in an ultrasonic bath. In specific periods of time, aliquots of the uppernatant were taken, filtered and analyzed by CE. The effect of the extraction time was evaluated by monitoring the peak area profile of the amines. By increasing the extraction time no significant differences in peak area were observed for MEA, DEEA, TEA and DCHA. However, for DEA and MCHA, a slight increase in peak area was observed at 20 min of extraction. Therefore, 20 min was selected for the extraction time.

Table 2
Analytical performance of the method regarding precision

Amine	Migration time (min)	Time, RSD (%)	Peak area, RSD (%)
MEA	4.38	0.48	1.4
DEA	5.39	0.48	1.1
MCHA	5.52	0.68	1.2
DEEA	5.67	0.51	1.8
TEA	5.97	0.50	1.3
DCHA	7.39	0.69	1.1

RSD: relative standard deviation (10 consecutive injections).

Table 3
Statistical parameters of the analytical curves and estimates of limits of detection (LOD) for the indirect UV-absorbance detection methodology

Amine	Analytical curve equation[a]	R	LOD[b] (mg L^{-1})
MEA	$Y = 0.433X + 0.451$	0.9989	1.27
DEA	$Y = 1.36X + 0.527$	0.9997	0.67
MCHA	$Y = 1.27X + 0.399$	0.9981	1.54
DEEA	$Y = 1.37X - 0.178$	0.9999	0.52
TEA	$Y = 0.923X + 0.289$	0.9998	0.54
DCHA	$Y = 0.744X + 0.712$	0.9987	1.49

MEA, monoethanolamine; DEA, diethanolamine, TEA, triethanolamine; DEEA, diethylethanolamine, MCHA, monocyclohexylamine; DCHA, dicyclohexylamine.

[a] Amine concentration interval from 2.5 to 20 mg L^{-1}; based on peak area.

[b] Calculated from interpolation of Y in the calibration curve ($Y - Y_b = 3s_b$, where Y_b is the intercept and s_b is the error associated to its estimate).

3.3. Method validation

The precision of the proposed method regarding peak area and migration time repeatability for 10 consecutive injections of the standard solution at 10 mg L^{-1} was estimated (Table 2). Overall repeatability was better than 2% RSD.

For quantitative purposes, analytical curves based on peak area versus concentration were built. The analytical curves consisted of five points and three replicate injections of standards at each concentration level were performed. The analytical curve equations and the limits of detection derived from the curve statistics are presented in Table 3. The results showed good linearity over the concentration range from 2.5 to 20 mg L^{-1} ($r > 0.99$). The method limits of detection for the amines under investigation were in the range of 0.52–1.54 mg L^{-1}.

Table 1
Recovery study

Amine	Procedure A			Procedure B		
	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)	Added (mg L^{-1})	Found (mg L^{-1})	Recovery (%)
MEA	20	16	80 ± 3	20	20	101 ± 4
DEA	9.9	8.2	83 ± 5	9.9	9.7	98 ± 0.8
MCHA	9.9	4.4	44 ± 1	9.9	9.6	97 ± 0.8
DEEA	8.9	5.4	61 ± 0.4	8.9	8.4	95 ± 1
TEA	10	8.6	86 ± 3	10	9.6	96 ± 1
DCHA	20	4.0	20 ± 1	20	19	95 ± 1

Procedure A employs toluene, procedure B employs a water–ethanol (90:10, v/v) solution.

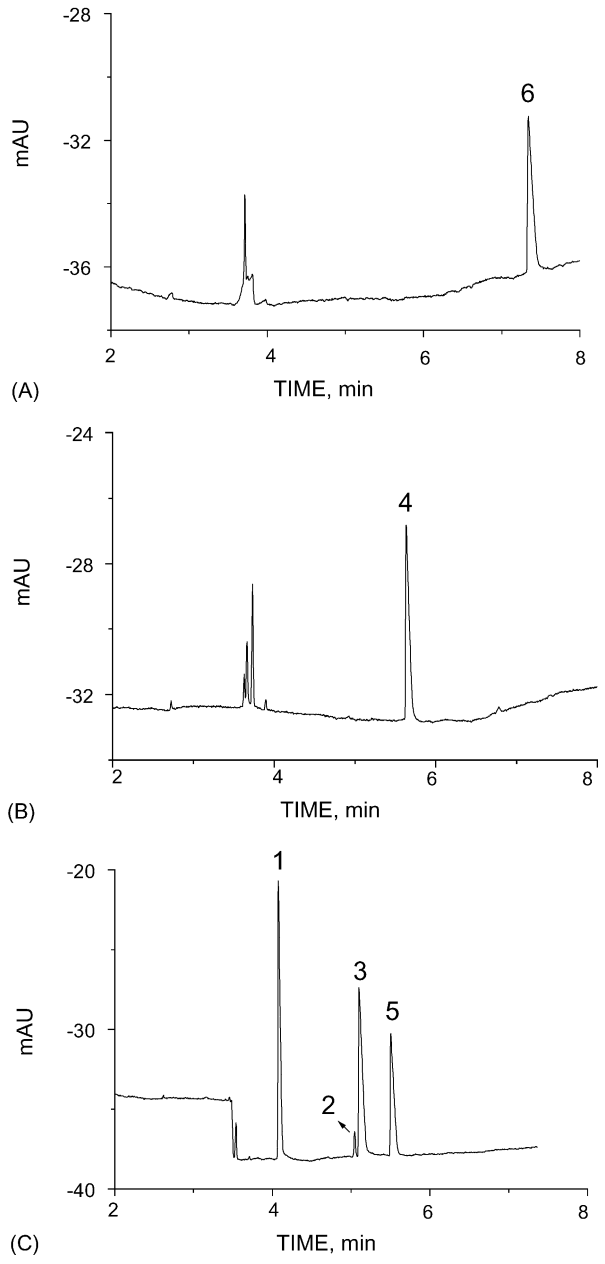

Fig. 3. Electropherograms of the ethanolic extracts of commercial products containing VCIs: (A) plastic sample, (B) paper sample and (C) foam sample. Electrophoretic conditions and peak labels as in Fig. 2.

3.4. Analysis of commercial products

Three commercial products (plastic, paper and foam) containing volatile corrosion inhibitors were analyzed by the proposed CE methodology. Samples were cut into pieces and extracted according to the optimized procedure using 10% ethanolic solution during 20 min. Dilution of the resulting extracts was necessary due to high concentration of amines in the original samples. Fig. 3 presents the electropherograms the sample ethanolic extracts. Identification of the compounds was performed using spiking techniques. The concentration of amines found in the commercial products are summarized in Table 4. According to the manufacturer, the nominal amount of volatile inhibitor present in treated paper, for instance, varies from 6 to 15% (w/w). The sample analyzed in the laboratory (sample B) presented a much lower concentration.

Table 4
Concentration of amines in the commercial products

Sample	Amine	Concentration (%, w/w)
Plastic	DCHA	0.050 ± 0.001
Paper	DEEA	1.79 ± 0.03
Foam	MEA	22.3 ± 0.25
	DEA	0.5 ± 0.01
	MCHA	7.5 ± 0.09
	TEA	7.1 ± 0.10

MEA, monoethanolamine; DEA, diethanolamine, DEEA, diethylethanolamine; TEA, triethanolamine; MCHA, monocyclohexylamine; DCHA, dicyclohexylamine.

4. Conclusion

A rapid, simple and efficient analytical method for determination of the most commonly found amine corrosion inhibitors used in wrapping materials has been developed. In comparison with chromatographic methodologies, the proposed CE method has the advantage that no derivatization procedure is required since the detection is performed indirectly. A few method validation parameters were established revealing good migration time repeatability and area repeatability, excellent linearity and adequate accuracy. The method was successfully applied to the analysis of commercial wrapping materials.

Acknowledgements

The authors wish to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) of Brazil for fellowships (FAPESP 02/10197-1, CNPq 301201/94-3) and financial support (FAPESP 00/04414-4 and 98/12385-2). The authors are also in dept with Dr. Arnaldo Alves Cardoso for allowing the use of his CE system, Mário Genovez (VCI Brasil), who kindly donated the amine standards and Maurício Correa (General Motors Brasil) for supplying the commercial products.

References

[1] V.S. Sastri, Corrosion Inhibitors: Principles and Applications, Wiley, New York, 1998.
[2] G. Trabanelli, V. Carassiti, in: M.G. Fontana, R.W. Staehle (Eds.), Advances in Corrosion Science and Technology, Plenum Press, New York, 1970, p. 186.
[3] G.E. Fodor, in: A. Raman, P. Labine (Eds.), Reviews on Corrosion Inhibitors Science and Technology, NACE International: The Corrosion Society, Houston, 1993, p. II-17-1.

[4] L.R.M. Estevão, R.S.V. Nacimento, Corros. Sci. 43 (2001) 1133.
[5] M.A. Quraishi, D. Jamal, Corrosion 58 (2002) 387.
[6] S.L. Abidi, J. Chromatogr. 213 (1981) 463.
[7] J. Pietsch, S. Hampel, W. Schmidt, H.J. Brauch, Fresenius J. Anal. Chem. 355 (1996) 164.
[8] F. Sacher, S. Lenz, H.J. Brauch, J. Chromatogr. A 764 (1997) 85.
[9] L. Pan, J.M. Chong, J. Pawliszyn, J. Chromatogr. A 773 (1997) 249.
[10] R.M. López, M.J. González, A.J.M. Ordieres, P.T. Blanco, J. Chromatogr. A 721 (1996) 231.
[11] L.I. Monser, G.M. Greenway, Anal. Chim. Acta 322 (1996) 63.
[12] G. Huhn, J. Mattusch, H. Schulz, Fresenius J. Anal. Chem. 351 (1995) 563.
[13] O. Busto, J. Guach, F. Borrull, J. Chromatogr. A 718 (1995) 309.
[14] T. Teerlink, M.W.T. Hennekes, C. Mulder, H.F.H. Brulez, J. Chromatogr. A 691 (1997) 269.
[15] W.S. Wu, B.S. Gaind, J. Liq. Chromatogr. 15 (1992) 267.
[16] O. Busto, M. Miracle, J. Guasch, F. Borrull, J. Chromatogr. A 757 (1997) 311.
[17] R. Lindahl, J.O. Levin, K.J. Anderson, J. Chromatogr. 643 (1993) 35.
[18] P. Jandera, K. Ventura, R. Hladoniková, J. Liq. Chromatogr. 17 (1994) 69.
[19] C.G. Fu, H.D. Xu, Analyst 120 (1995) 1147.
[20] T. Matsumoto, T. Tsuda, Trends Anal. Chem. 9 (1990) 292.
[21] B. Kersten, Chromatographia 34 (1992) 607.
[22] I.M. Krasnova, I.V. Kolmakova, L.A. Kartsoka, J. Anal. Chem. 52 (1997) 767.
[23] R.D. Rocklin, M.A. Rey, J.R. Stillian, L. Campbell, J. Chromatogr. Sci. 27 (1998) 474.
[24] J.R. Larson, C.D. Pfeiffer, Anal. Chem. 55 (1983) 393.
[25] W. Beck, H. Engelhardt, Chromatographia 33 (1992) 313.
[26] J.M. Riviello, M.P. Harrold, J. Chromatogr. A 652 (1993) 385.
[27] Y. Mori, K. Ueno, Y. Umeda, J. Chromatogr. A 757 (1997) 328.
[28] W.H. Matchett, W.C. Brumley, J. Liquid Chromatogr. Rel. Technol. 20 (1997) 79.
[29] K.D. Altria, M. Wallberg, D. Westerlund, J. Chromatogr. B 714 (1998) 104.
[30] C.S. Chiou, J.S. Shih, Anal. Chim. Acta 360 (1998) 69.