

Ion-chromatographic determination of inorganic anions and cations in some reagents used in the electronics industry[☆]

Pier Luigi Buldini^{*}, Jawahar Lal Sharma^{☆☆} and Shikha Sharma^{☆☆☆}

C.N.R.-LAMEL, Laboratorio Analisi Chimica Materiali, Via Idraulico 17/2, I-40138 Bologna (Italy)

(First received September 21st, 1992; revised manuscript received June 10th, 1993)

ABSTRACT

In the electronics industry, wafer cleaning is usually performed by means of hot ammoniacal or acidic hydrogen peroxide solutions, which remove organic surface films by oxidative breakdown and dissolution to expose the substrate surface for concurrent and/or subsequent decontamination reactions. It is difficult to establish the optimum renewal cycle of the cleaning solutions to avoid economic as well as pollution problems. The present work deals with the application of ion chromatography to the determination of anionic as well as cationic impurities in hydrogen peroxide and ammonia, which are extensively used in wafer cleaning technology. As these two reagents cannot be injected directly into the separator column, methods are suggested for the pretreatment of the samples. Hydrogen peroxide was subjected to UV photolysis for about 30 min in an UV digester at $85 \pm 5^\circ\text{C}$. Though ammonia could also be treated in the same manner, simply heating it at $85 \pm 5^\circ\text{C}$ for 45 min in a dust-free cell, to expel most of the ammonia as gas, was found to be satisfactory. The samples were then analysed by ion chromatography and were found to contain chloride, phosphate, sulphate, copper, zinc, iron and manganese as impurities in variable amounts, when analysed at different stages of the wafer cleaning operation (20–1000 $\mu\text{g/l}$).

INTRODUCTION

Clean surfaces in the fabrication of semiconductor devices are important as a number of processes are highly sensitive to impurities present in the chemicals employed [1]. One of the commonest methods of silicon wafer cleaning and/or photoresist stripping is treatment of the surface with a mixture of hydrogen peroxide and

ammonia, followed by a second peroxide treatment at low pH. This is intended to remove any organic surface film by oxidative breakdown and dissolution to expose the silicon or its oxide surface free from organic matter for concurrent or subsequent decontamination reactions. Metallic impurities, whose levels in the bath increase as more wafers are cleaned, are absorbed on the wafer surface and have proved to cause yield and reliability problems in electronic devices [2]. Contrary to this, the modern trend in semiconductor device evolution is to employ very large or ultra-large scale integration (VLSI or ULSI) technology, which in turn emphasizes the requirement for very pure chemicals, resulting in lower defect densities and improved yields [3]. In addition, it is difficult to establish the optimum renewal time of the cleaning solutions with consequent economic as well as pollution prob-

^{*} Corresponding author.

^{*} Presented at the *International Ion Chromatography Symposium 1992, Linz, September 21–24, 1992*. The majority of the papers presented at this symposium were published in *J. Chromatogr.*, Vol. 640 (1993).

^{**} Permanent address: K.M. College, University of Delhi, Delhi 110007, India.

^{***} Permanent address: Satyawati Sood School, Nizamuddin East, Delhi 110041, India.

lems, which leads to strict control of impurities in many process steps in order to reduce chemical consumption and waste.

Several techniques, such as flame or flameless atomic absorption spectrometry [4,5], inductively coupled plasma atomic emission spectrometry [6], polarography [7,8], spark source mass spectrometry [9] and inductively coupled plasma mass spectrometry [10], have been suggested for the determination of impurities in ultra-pure reagents. Most of these techniques are based on preconcentration of impurities and/or addition of one or more reagents to the sample prior to analysis, while others require very expensive equipment and highly skilled personnel.

Ion chromatography, introduced by Small *et al.* [11], is one of the simplest and most effective techniques to determine both anionic as well as cationic impurities owing to its high sensitivity, rapidity and ease of operation coupled with the advantage of simultaneous determinations. Dulski [12] determined some anions in hydrofluoric and nitric acids, while Murayama *et al.* [13] determined bromide, nitrate and sulphate in several acids by concentrating these anions on a chromatographic column.

The present work deals with the application of ion chromatography for the determination of fluoride, chloride, phosphate, sulphate, copper(II), cadmium(II), lead(II), zinc(II), iron(III), nickel(II), cobalt(II) and manganese(II) in hydrogen peroxide, ammonia and their mixtures without any preconcentration of the impurities or addition of reagents. The method has been successfully used for monitoring the process media employed for the cleaning of semiconductor wafers.

PRELIMINARY STUDIES

Hydrogen peroxide

The chemistry of hydrogen peroxide has been extensively studied [14–16]. It is a strong oxidizing agent in acidic as well as in alkaline conditions. At room temperature the half-life of acidic (pH 4.5) and alkaline (pH 9.0) hydrogen peroxide is about 50 h and 11 h, respectively. The stability of hydrogen peroxide solutions decreases with an increase in temperature as well

as pH. By heating at only $85 \pm 5^\circ\text{C}$, the relative hydrogen peroxide content of the acidic solution (pH 4.5) was found to decrease by 99% in 60 min and by more than 99.9% in 90 min.

When the hydrogen peroxide solution was subjected to UV irradiation at $85 \pm 5^\circ\text{C}$, the relative content of the acidic solution was found to be less than 1% in 15 min and less than 0.1% in 20–25 min. For the alkaline solution (pH 9.0) the corresponding values were found 5 and 11 min, respectively. As hydrogen peroxide cannot be injected directly on the separator column, UV photolysis permits its analysis without any reagent addition.

Recoveries obtained with spiked samples range between 97 and 103% for all the impurities under investigation.

Ammonia

Though ammonia could also be treated in the same manner as hydrogen peroxide, simply heating it at $85 \pm 5^\circ\text{C}$ for 45 min in a dust-free cell, to expel most of the ammonia as gas, was found to be satisfactory. Heating was performed in PTFE containers fitted with 29/32 sockets and PTFE heads with 29/32 cones, adapted for passing inert gas through the cell and for water circulation, in order to avoid any eventual loss due to formation of micro-droplets.

By using spiked samples, recoveries of various ions were found to range between 97 and 103%.

EXPERIMENTAL

Reagents and standards

Sodium carbonate, sodium hydrogencarbonate, oxalic acid, lithium hydroxide, 4-(2-pyridylazo)-resorcinol monosodium salt (PAR) and pyridine-2,6-dicarboxylic acid (PDCA) were chromatographic grade (Novachimica, Milan, Italy), hydrogen peroxide (30% m/m, without stabilizer), ammonium hydroxide (30%), sodium hydroxide, glacial acetic acid and nitric acid (70%) were Erbaton electronic grade (Carlo Erba Reagenti, Milan, Italy), and sulphuric acid was analytical grade (Carlo Erba Reagenti). Ammonium acetate (2 M, pH 5.5) was chelation grade (Dionex, Sunnyvale, CA, USA). Ultra-pure water with conductivity $<0.1 \mu\text{S}$ (DI water)

was obtained from a Milli-Q (Millipore, Bedford, MA USA) four-bowl deionization system.

Working standards were prepared daily by diluting Carlo Erba Reagenti Normex atomic absorption standards (1.000 g/l) or by dissolving the required Carlo Erba Reagenti analytical-grade reagents.

Quartz test tubes and all glassware were cleaned in concentrated nitric acid and carefully washed with DI water. Normal precautions for trace analysis were observed throughout.

Instrumentation

Hydrogen peroxide samples were subjected to UV photolysis in a Metrohm (Herisau, Switzerland) 705 UV digester equipped with a 500-W high-pressure mercury lamp. The temperature of the sample was maintained at $85 \pm 5^\circ\text{C}$ with the aid of a combined air/water cooling system.

Ammonia samples were heated in PTFE tubes fitted with 29/32 sockets, by employing a Berghof (Tübingen, Germany) sample evaporating device equipped with an aluminium heating block (in which the PTFE tubes can be inserted) whose temperature was maintained with the help of a T-P regulator (Berghof). The device was

also fitted with PTFE heads with 29/32 cones, adapted for passing inert gas and circulating running water to maintain low temperature to avoid any loss due to the transportation of micro-droplets by the vapour formed.

Chromatographic analyses were performed on a Dionex (Sunnyvale, CA, USA) 2000i ion chromatograph equipped with an EDM eluent degassing module, a GPM gradient pump, an IonPac AG9 guard column and an IonPac AS9 separator column (for anions), an AMMS anion micromembrane suppressor, an IonPac CG5 guard column and an IonPac CS5 separator column (for cations), an IonPac MRAD membrane reactor coupled with a reagent delivery module for post-column reagent addition and a CDM conductivity detector and a VDM2 UV-visible absorbance detector.

All measurements were made at $25 \pm 1^\circ\text{C}$ and, in all cases, injection of the sample was done at least in triplicate.

Peak areas were obtained using AI-450 Dionex software and background correction was applied wherever necessary.

All the chromatographic conditions are listed in Table I.

TABLE I
ION CHROMATOGRAPHIC CONDITIONS

	Anions	Cations
Column	IonPac AS9 (+AG9)	IonPac CS5 (+CG5)
Eluent	2.0 mM Na_2CO_3 + 0.75 mM NaHCO_3	50 mM $(\text{COOH})_2$ + 95 mM LiOH 95 mM LiOH (pH 4.8) or [for Fe(III) only] 6 mM PDCA + 90 mM CH_3COOH + 40 mM NaOH (pH 4.6)
Eluent flow-rate	1.5 ml/min	1.0 ml/min
Injection volume	25 μl	25 μl
Detection	Suppressed conductivity	Visible absorbance
Suppressor	AMMS	—
Regenerant	25 mM H_2SO_4	—
Regenerant flow-rate	8 ml/min	—
Post-column reagent	—	0.2 mM PAR in 3 M NH_4OH + 1 M CH_3COOH
Post-column reagent flow-rate	—	0.5 ml/min
Wavelength	—	520 nm

During the determination of cations, the eluent flow-rate was maintained at 1.0 ml/min and the post-column reagent flow-rate was 0.5 ml/min, and the total flow-rate (1.5 ml/min) was checked at the exit of the waste line. For optimal signal-to-noise ratio, the output was measured at a wavelength of 520 nm.

Samples preparation

Hydrogen peroxide. Aliquots of 5-ml of hydrogen peroxide or a mixture of hydrogen peroxide and ammonia were placed in quartz tubes and closed with conical PTFE stoppers that tapered to a point. The stoppers acted as cooling fingers, and thus prevented solution losses and also protected samples against contamination. The sample was subjected to UV photolysis at $85 \pm 5^\circ\text{C}$ for 30 min. The volume was made up to the original value with DI water, to compensate for the water loss due to evaporation, and analysed by ion chromatography for determining anionic impurities. For the determination of cationic impurities, 10 μl of 2 M nitric acid were added to ensure the dissolution of all the metallic oxides, if formed during the course of UV

photolysis, followed by the addition of 200 μl of 2 M ammonium acetate to maintain the sample pH in the range between 5 and 6, prior to chromatographic analysis. The volume was made up to 5 ml with DI water and analysed.

Ammonia. Aliquots of 5 ml of ammonia were heated at $85 \pm 5^\circ\text{C}$ in the sample heating device in an atmosphere of nitrogen for 45 min to reduce the volume to almost half. The volume was made up to the original value with DI water, and analysed for determining anionic impurities. For the determination of cationic impurities, 10 μl of 2 M nitric acid were added to ensure the dissolution of all the cationic species. The pH of the sample was maintained in the range 5–6 by adding 200 μl of 2 M ammonium acetate. The volume was made up to 5 ml with DI water and analysed by injecting on to the ion chromatograph.

RESULTS AND DISCUSSION

Figs. 1–3 show the chromatograms of a mixture of hydrogen peroxide and ammonia (1:1, v/v) for anion and cation determination.

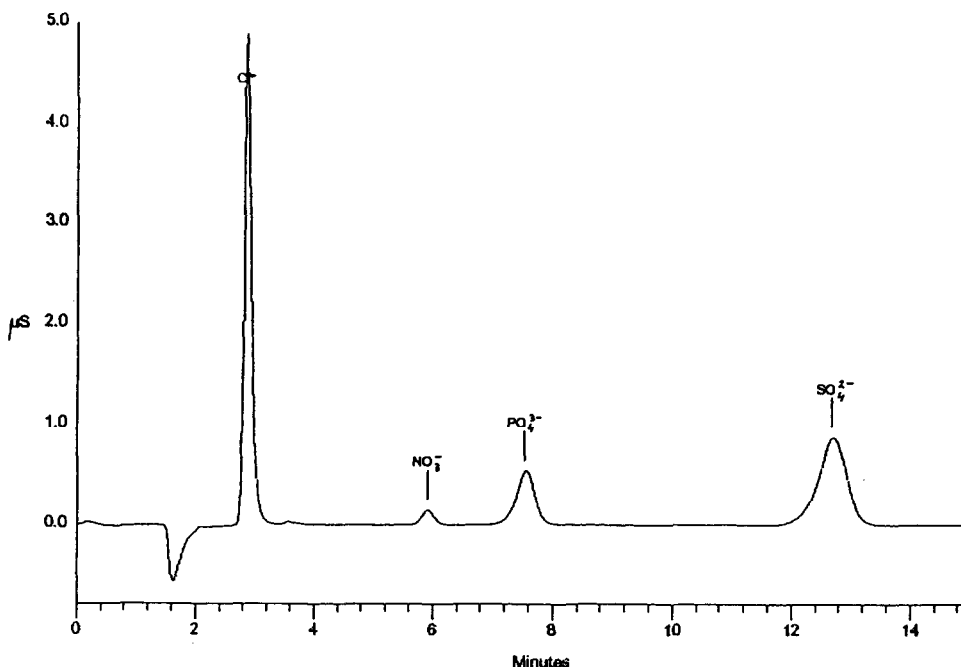


Fig. 1. Determination of anions in a mixture of ammonia and hydrogen peroxide (1:1, v/v) (exhausted batch). Chromatographic conditions as reported in Table I. Chloride 850 $\mu\text{g/l}$, sulphate 200 $\mu\text{g/l}$ and phosphate 120 $\mu\text{g/l}$.

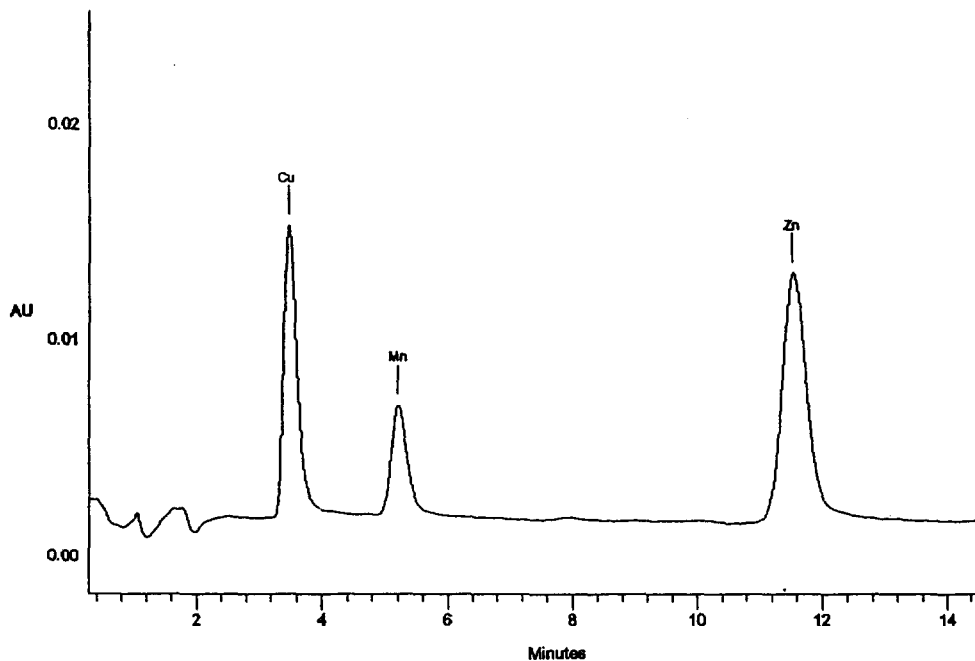


Fig. 2. Determination of cationic impurities in a mixture of ammonia and hydrogen peroxide (1:1, v/v) (exhausted batch). Chromatographic conditions as reported in Table I. Copper(II) 240 $\mu\text{g/l}$ and zinc(II) 380 $\mu\text{g/l}$.

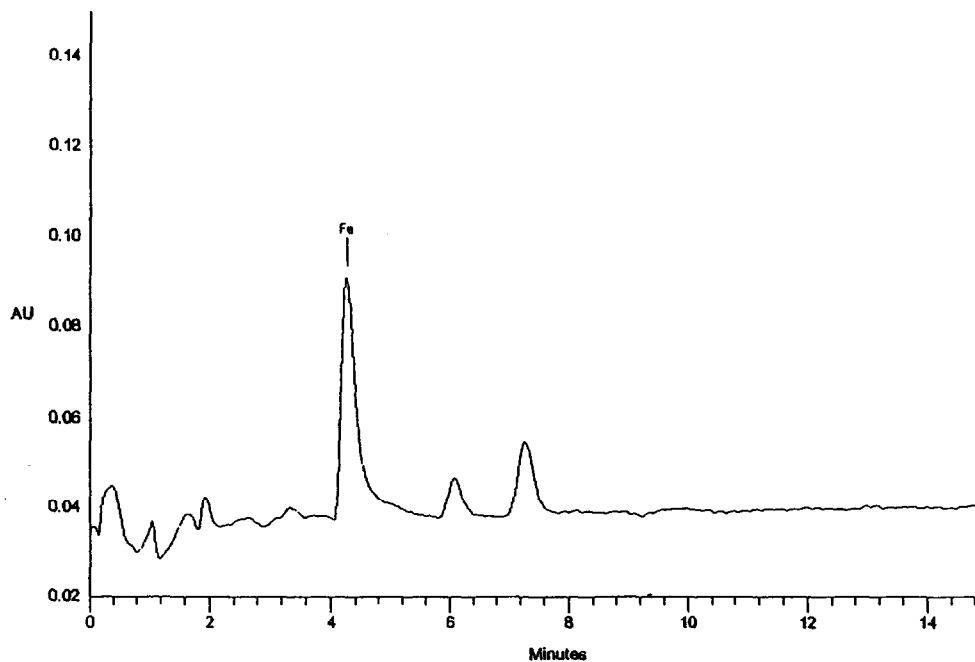


Fig. 3. Determination of iron(III) in a mixture of ammonia and hydrogen peroxide (1:1, v/v) (exhausted batch). Chromatographic conditions as reported in Table I. Iron(III) 950 $\mu\text{g/l}$.

It is evident that the detection of the various species in these reagents is straightforward. Lead(II) and cadmium(II) cannot be determined with PDCA eluent because these ions are so strongly bound to PDCA that they are not sensitively detected by PAR. Similarly, iron cannot be determined with oxalate eluent, while zinc(II), nickel(II) and cobalt(II) can be determined by either of the two eluents. For convenience, oxalate eluent was used for all the cations except iron, which was determined by PDCA eluent.

In the case of cation determination using oxalate eluent, normally the peak appearing just before lead(II) (at about 2.5 min) becomes larger if the matrix is very rich in various ions, and interferes with its determination. Employing the described sample pretreatment procedure, the size of this peak becomes vanishingly small and lead(II) can be detected in very low amounts, as reported in Table II.

The described ion chromatographic procedure, using the oxalate eluent, suffers from the drawback that cadmium(II) and manganese(II) have retention times very close to each other and therefore coelute with each other, so preventing their simultaneous determination, but the prob-

lem is resolved by the use of the PDCA eluent, as this gives a peak only for manganese(II).

The detection limits and concentration ranges in which calibration curves are linear with correlation coefficients greater than 0.99 are shown in Table II.

The effect of UV radiation on various anions and cations in the presence of hydrogen peroxide as well as a mixture of hydrogen peroxide and ammonia was investigated in detail. Deionized water as well as acidic and alkaline hydrogen peroxide samples were spiked with varying amounts of many common anions and heavy/transition metal ions and subjected to UV photolysis for 4 h prior to chromatographic analysis.

As shown in Tables III and IV, it was found that fluoride, chloride, bromide, phosphate and sulphate anions and copper(II), cadmium(II), lead(II), zinc(II), iron(III), nickel(II) and cobalt(II) cations were not affected by UV photolysis and the recovery of these species was between 97 and 103% in deionized water as well as in acidic or alkaline hydrogen peroxide samples. In the case of iodide, nitrite, nitrate and manganese(II) the recoveries were not quantitative. This is because UV photolysis of hydrogen peroxide proceeds via a radical mechanism. The

TABLE II

DETECTION LIMITS AND USEFUL CONCENTRATION RANGES IN HYDROGEN PEROXIDE AND AMMONIA BY ION CHROMATOGRAPHY, AFTER SAMPLE PRETREATMENT

Ion	Eluent	Detection limit ($\mu\text{g/l}$)	Range ($\mu\text{g/l}$)
F^-	Carbonate–hydrogencarbonate	5	10–5000
Cl^-	Carbonate–hydrogencarbonate	10	20–4000
Br^-	Carbonate–hydrogencarbonate	15	40–4000
PO_4^{3-}	Carbonate–hydrogencarbonate	25	50–5000
SO_4^{2-}	Carbonate–hydrogencarbonate	25	50–5000
Cu(II)	Oxalate	5	10–1500
Cd(II)	Oxalate	25	50–2500
Pb(II)	Oxalate	10	25–2500
Zn(II)	Oxalate	10	25–2500
Fe(III)	PDCA	5	15–2000
Ni(II)	Oxalate	20	100–1500
Co(II)	Oxalate	10	20–2000
Mn(II)^a	Oxalate	10	25–1500

^a Valid for ammonia only.

TABLE III

RECOVERY OF TRACE ANIONS IN 30% (m/m, WITHOUT STABILIZER) HYDROGEN PEROXIDE AND (30%) AMMONIA

Mean of the values obtained for ten samples —triplicate injection each. Chromatographic conditions as previously reported in Table I.

Anion	Added (ppm)	Hydrogen peroxide			Ammonia		
		Found (ppm)	Recovery (%)	R.S.D. (%)	Found (ppm)	Recovery (%)	R.S.D. (%)
Fluoride	0.000	0.000	—	—	0.000	—	—
	0.100	0.103	103	3.0	0.102	102	2.1
	0.500	0.508	101.6	1.9	0.509	101.8	2.0
Chloride	0.000	0.042	—	2.0	0.064	—	1.7
	0.100	0.144	102	2.0	0.166	102	2.0
	0.500	0.548	101.2	1.5	0.572	101.6	1.8
Bromide	0.000	0.000	—	—	0.000	—	—
	0.100	0.102	102	2.0	0.098	98	2.1
	0.500	0.496	99.2	1.1	0.508	101.6	1.9
Nitrite	0.000	0.042	—	15.4	0.017	—	19.6
	0.100	0.096	54	24.9	0.092	75	33.2
	0.500	0.366	65	18.6	0.434	83	22.5
Nitrate	0.000	0.021	—	22.6	0.062	—	37.9
	0.100	0.059	38	31.5	0.157	97	28.9
	0.500	0.328	61.4	37.2	0.555	98.6	33.3
Phosphate	0.000	0.085	—	2.2	0.024	—	1.5
	0.100	0.188	103	3.0	0.122	98.4	1.8
	0.500	0.592	101.2	1.5	0.528	100.7	1.0
Sulphate	0.000	0.034	—	1.5	0.054	—	1.7
	0.100	0.135	101	1.2	0.152	98	2.0
	0.500	0.539	101	1.2	0.561	101.3	1.5

$\cdot\text{OH}$ radicals formed during the irradiation interact with the mentioned species and give a number of reaction products depending upon the temperature, medium and concentration of the $\cdot\text{OH}$ radicals [17,18]. Thus, the sample pretreatment employing UV photolysis is not recommended for the determination of iodide, nitrate, nitrite and manganese(II).

CONCLUSIONS

Ion chromatography has been found to be very effective for determining anionic as well as cationic impurities in hydrogen peroxide and ammonia.

These reagents were found to contain chloride, nitrate, phosphate and sulphate as anionic impurities and iron, copper and zinc as cationic impurities. The technique has been successfully applied for determining the impurities in mixtures of hydrogen peroxide and ammonia, and can therefore be used for monitoring trace levels of various anions and cations in baths for semiconductor cleaning.

ACKNOWLEDGEMENT

Two authors (J.L.S. and S.S.) are grateful to the International Centre for Theoretical Physics (Trieste, Italy) for awarding them a fellowship.

TABLE IV

RECOVERY OF TRACE CATIONS IN 30% (m/m, WITHOUT STABILIZER) HYDROGEN PEROXIDE AND (30%) AMMONIA

Mean of the values obtained for ten samples —triplicate injection each. Chromatographic conditions as reported in Table I.

Cation	Added ($\mu\text{g/l}$)	Hydrogen peroxide			Ammonia		
		Found (ppm)	Recovery (%)	R.S.D. (%)	Found (ppm)	Recovery (%)	R.S.D. (%)
Pb(II)	0.000	0.000	—	—	0.000	—	—
	0.050	0.051	102	2.1	0.051	102	2.0
	0.100	0.101	101	1.7	0.102	102	2.2
Cd(II) ^a	0.000	0.000	—	—	0.000	—	—
	0.050	0.051	102	2.0	0.051	102	2.0
	0.100	0.101	101	1.3	0.102	102	2.1
Fe(III)	0.000	<0.010	—	—	<0.010	—	—
	0.050	0.059	100	0.5	0.060	101	1.6
	0.100	0.110	100	0.5	0.112	102	2.1
Cu(II)	0.000	0.012	—	1.6	0.017	—	1.9
	0.050	0.063	102	2.0	0.068	102	2.1
	0.100	0.114	102	2.2	0.119	102	2.0
Ni(II)	0.000	0.000	—	—	0.000	—	—
	0.100	0.098	98	2.0	0.98	98	2.0
	0.500	0.510	102	2.0	0.500	100	1.5
Zn(II)	0.000	<0.020	—	—	<0.020	—	—
	0.050	0.068	100	1.3	0.065	100	1.5
	0.100	0.119	100	1.5	0.118	101	2.0
Co(II)	0.000	0.000	—	—	0.000	—	—
	0.050	0.049	98	2.0	0.051	102	2.0
	0.100	0.100	10	1.0	0.101	101	1.5
Mn(II) ^a	0.000	0.000	—	—	<0.025	—	—
	0.050	0.042	84	3.5	0.075	100	1.0
	0.100	0.088	88	4.8	0.125	100	1.0

^a Cadmium(II) and manganese(II) not determined simultaneously.

REFERENCES

- G. Gould and E.A. Irene, *J. Electrochem. Soc.*, 134 (1987) 1031.
- M. Heyns, *Microcontamination*, 9 (1991) 29.
- H.J. Rath and R. Neuteufel, in B.O. Kolbesen, D.V. McCaughan and W. Vandervorst (Editors), *Analytical Techniques for Semiconductor Materials and Process Characterization*, The Electrochemical Society, Pennington, NJ, 1990, p. 335.
- E. Ivanova, I. Havezov, N. Vracheva and N. Jordanov, *Fresenius' Z. Anal. Chem.*, 320 (1985) 133.
- F.J. Langmyhr and J.T. Haekedal, *Anal. Chim. Acta*, 83 (1976) 127.
- R.N.P. Farrow, *Anal. Proc.*, 24 (1987) 178.
- P.L. Buldini and D. Ferri, *Microchim. Acta*, 1 (1980) 423.
- V.A. Stenger, J.D. McLean and R.M. Van Effen, *Anal. Chem.*, 57 (1985) 27A.
- T.A. Chanysheva, I.R. Shelpakova, A.I. Saprykin, L.M. Yankovskaya and I.G. Yudelevich, *Zh. Anal. Khim.*, 38 (1983) 979.
- P.J. Paulsen, E.S. Beary, D.S. Bushee and J.R. Moody, *Anal. Chem.*, 60 (1988) 971.
- H. Small, T.S. Stevens and W.C. Bauman, *Anal. Chem.*, 47 (1975) 1801.
- T.R. Dulski, *Anal. Chem.*, 51 (1979) 1439.
- M. Murayama, M. Suzuki and S. Takitani, *J. Chromatogr.*, 466 (1989) 355.

- 14 W.C. Schumb, C.N. Satterfield and R.L. Wentworth, *Hydrogen Peroxide*, Reinhold., New York, 1955.
- 15 J.W. Faust Jr., in H.C. Gatos (Editor), *Surface Chemistry of Metals and Semiconductors*, Wiley, New York, 1960, p. 151.
- 16 R.P.S. Black and A.T. Hawkinson, *Symposium on Cleanliness and Materials Processing for Electronic and Space Applications* (ASTM STP, No. 342), American Society for Testing and Materials, Philadelphia, PA, 1962, p. 87.
- 17 R.W. Glass and T.W. Martin, *J. Am. Chem. Soc.*, 92 (1970) 5084.
- 18 A. Farkas and L. Farkas, *Trans. Faraday Soc.*, 34 (1938) 1113, 1120.