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Short communication

In situ matrix evaporation by isothermal distillation of high-purity reagents for the determination of trace impurities by ion chromatography

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Abstract

In situ matrix evaporation of high-purity acids based on isothermal distillation was achieved in a high-density polyethylene (HDPE) container on a water bath, to avoid contamination from the laboratory environment. The solubility of water and acid vapours in glycerol due to co-association was utilized to achieve complete evaporation. All major sources which contribute to the process blank were taken care of in a simple and effective way. A 50-fold preconcentration with >99.9% matrix removal was achieved for the analysis of low-boiling acids, HCl, HF, HNO_3 and H_2O_2. The non-volatile ions NH_4^+, Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-} and PO_4^{3-} were determined by ion chromatograph with conductivity detection. The detection limits were 6–130 ng/l with recoveries of 85–110% for all ions studied.

Keywords: Sample preparation; In situ matrix evaporation; Suprapur acids; Trace ions

1. Introduction

The purity of reagents such as HF, HCl, HNO_3 and H_2O_2 used in the wafer cleaning operation in semiconductor industries has a direct impact on device and yield reliability [1]. Various sensitive techniques like inductively coupled plasma mass spectrometry (ICP-MS) [2] and ion chromatography (IC) [3] require both matrix separation and preconcentration prior to the analysis of such high purity reagents. IC has gained wide spread acceptance as an analytical technique for the determination of various ionic species. The most challenging samples for analysis by IC are those in which the analyte is present at low concentration in a sample matrix of high ionic strength or of extreme pH. The widely used approach to overcome this problem is either dilution of the matrix [4–7] or by pretreatment (without preconcentration) of the matrices like H_2O_2 [8] and HF [9] before injection on to the column. With the dilution approach, the analytes of interest are also diluted and hence lower detection limits are not possible. In order to improve detection limit, the IC methods based on membrane suppressor [10], auto neutralization [11] and ion exclusion column [12] have recently been developed for the determination of sensitive impurities in non-oxidative acids. However, for extreme low-level determination of less sensitive phosphate and sulfate, apart from matrix separation, preconcentration is also essential. Generally, the analysis of high purity acids is achieved by evaporating the acids either in a laminar flow hood or in closed plastic chambers purged continuously with the filtered air. In these processes, there is always a risk of contamination of analyte due to long exposure to the laboratory environment [13] further, the evaporation of large quantity of acid may contaminate the clean laboratory environment. To overcome these problems, there is a need for in situ matrix evaporation system. So far, no such system has been reported in the literature.

Isothermal distillation has been used for the preparation of high purity acids [13], separation of matrices (arsenious oxide

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[14] and boric acid [15]) and traces of analyte [16]. In the present work, an in situ matrix evaporation system has been developed in which glycerol was used to absorb acid vapours produced during the evaporation. The developed method was applied for ion chromatographic determination of traces of cationic (NH_4^+, Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) and anionic (SO_4^{2-} and PO_4^{3-}) impurities in a variety of matrices (HCl, HF, HNO_3 and H_2O_2).

2. Experimental

2.1. General precautions

Vinyl gloves were worn throughout all the steps of the process. Care was taken to minimise contaminants and the sample containers used were thoroughly leached and rinsed with the deionised water.

2.2. Reagents and sample

All solutions were prepared in 18 MΩ cm water, obtained from milli-Q system (Millipore, Bedford, MA, USA). All standard stock solutions (1 mg/ml) were prepared by dissolving corresponding AR grade salts in DI water. Working standard solutions were prepared daily by required dilutions of stock solution prior to use. Suprapur grade sodium hydroxide (Merck, Germany), methane sulfonic acid (Loba Chemie, India) and AR grade glycerol (SD Fine Chemicals, India) were used. HCl and HF samples of Suprapur grade (E-Merck, Germany), HNO_3 and H_2O_2 samples of AR grade (E-Merck, India) were taken for the analysis. HDPE containers (Laxbro, India) were used for the storage of standard solution.

2.3. Apparatus

In situ matrix evaporation was carried out in 500 ml (outer) and 65 ml (inner) capacity HDPE containers (Fig. 1).

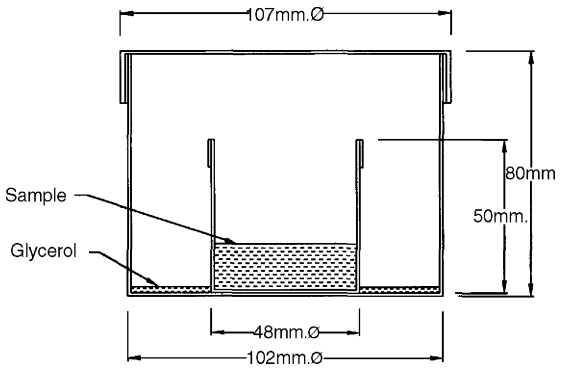

Fig. 1. In situ matrix evaporation assembly.

2.4. Instrumentation and chromatographic conditions

Chromatographic analysis was performed on a DX-300 ion chromatograph (Dionex, Sunnyvale, USA). The system consists of an advanced gradient pump (AGP-1), a liquid chromatography module (LCM-3) and a conductivity detector (CDM-3). Data acquisition and processing was carried out using a personal computer equipped with chromatography software (Aimil Winacds 6.2, Mumbai, India). All the columns used in this study were from Dionex. For the separation of anions an IonPac AG17 guard column (50 mm × 4 mm) and IonPac AS17 (250 mm × 4 mm) analytical column were used. The eluent was NaOH (15 mM) at a flow rate of 1 ml/min. For cationic separation, an IonPac CG12 (50 mm × 4 mm) guard column and IonPac CS12 (250 mm × 4 mm) analytical column were utilized, which provides fast separation of monovalent and divalent cations. Methane sulfonic acid (25 mM) was used as eluent at flow rate of 1 ml/min. The injection volumes for determination of anions and cations were 100 and 25 μl, respectively. For suppression of the conductivity due to eluents, anion self regenerating suppressor (ASRS, 4 mm) and cation self regenerating suppressor (CSRS, 4 mm) from Dionex were used in the IC analysis.

2.5. Sample pretreatment

The HDPE vessel containing 25 ml of sample solution was kept in side an outer HDPE vessel containing ∼50 ml of glycerol (Fig. 1). The tightly capped outside vessel was kept on a water bath (∼90 °C) for ca. 6 h for the complete removal of matrix. To remove the traces of acid, the procedure was repeated with fresh glycerol solution (∼25 ml) for ca. 1 h. The sample vessel was taken out carefully and capped immediately. The outer surface of the sample container was thoroughly cleaned. The traces of ion residues were dissolved in 0.5 ml of DI water. The solution was injected into the IC for separation and detection of ionic impurities. Quantification of trace impurities was carried out by an external calibration. The analysis of process blank was also carried out by similar procedure.

3. Result and discussion

3.1. Assessment of in situ matrix evaporation system performance

In open evaporation, the acid vapours are continuously removed from the system and hence favours liquid–vapour equilibrium in the forward direction to complete the evaporation process. In the proposed system, continuously produced acid vapours from the inner sample container are absorbed into the glycerol present in the outer vessel. The absorption of binary mixture (acid and water vapours) is mainly due to their solubility in glycerol, further the enhancement of solubility of the binary mixture in glycerol is due to co-association (inter molecular hydrogen bonding between two dissimilar

molecules [17]). The solubility of acids has been confirmed by the titration of glycerol acid mixture (obtained through procedure) versus standard alkali. The free acid (HCl and HF) in glycerol was almost same as that initially taken in the inner container. But in the case of nitric acid only 30% of free acid was found in the glycerol, this is due to chemical reaction [18] of nitric acid with glycerol (oxidation of glycerol by nitric acid). Since the IC is very susceptible to high ionic strength, second distillation with fresh glycerol was carried out to remove any traces of liquid in the inner container. Ultimately, the procedure leads to peconcentration of trace ions with a very lower ionic strength (pH 3–4). The sample solution thus obtained can be analyzed by ion chromatograph. Since the time of evaporation depends on sample size, wall thickness and thermal conductivity of the inner vessel, it has to be optimized during individual experiments.

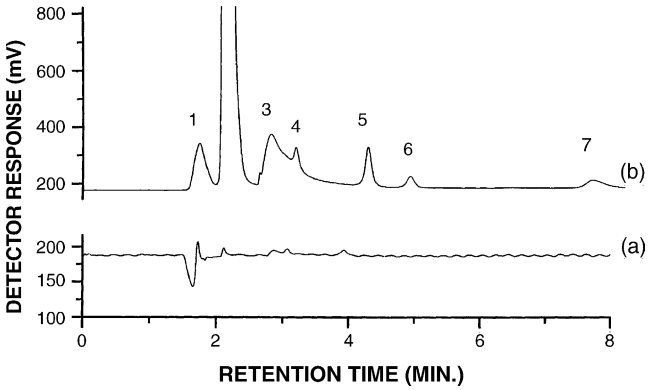

Fig. 2. (a) Profile obtained for the process blank for anions. (b) Chromatogram obtained for the trace anions in suprapur HCl (30%) after matrix evaporation and preconcentration (50 times, 25 ml:0.5 ml in water). Peaks: (1) CH_3COO^- (not quantified); (2) Cl^- (matrix); (3) Br^- (not quantified); (4) NO_3^- (not quantified); (5) SO_4^{2-} 720 (μg/l); (6) $C_2O_4^{2-}$ (not quantified); (7) PO_4^{3-} (1057 μg/l). Sample injection volume is 100 μl.

3.2. Process blank

The four major contributions to the process blanks are the environment, reagent, leaching of impurities from digestion vessel, and the skill of the analyst carrying out the procedure [19]. In the present procedure, the closed container provides the clean environment for the analyte. As the whole experiment is carried out on water bath, (poly (4-methyl-1-pentene), PP, TPX) vessels, which are less expensive than and superior to the Teflon and Vycor vessels, can be used with minimum leaching of impurities [20]. The skill of analyst, which is the most difficult component to evaluate, has also been taken care of to a large extent because the analyst performs lesser and simpler operations for the sample preparation. As a result, this evaporation procedure leads to very low process blank.

3.3. LOD and recovery study

The limit of detection (3σ) was determined by injecting the process blank into IC and the standard deviations ($n = 5$) were calculated for all the analytes. For all the sample solutions, it was calculated based on the preconcentration factor of 10 (10 → 1 ml) and the LOD's for different analytes are given in Table 1. The limit of quantification (10σ) of this method is substantially below the maximum limit of impurities as specified by the manufacturer for these reagents. In this matrix separation process, more than 99.9% of matrix was removed. It was imperative to study the recovery behavior of trace analytes. The each matrix (HF, HCl, HNO_3 and H_2O_2) was spiked with 20–1000 ng (0.5–100 μg for H_2O_2) of the cations, 1000 ng of sulfate and phosphate (100 μg for H_2O_2), evaporated through the procedure and then analyzed by ion chromatograph. The recoveries of analytes ranged between 85 and 110% (Table 1). During the conventional evaporation on hot plate, extreme precaution is needed at the dehydration stage mainly due to sudden increase of temperature leads to the formation of condensed phosphate from orthophosphate [21]. In the present system, since the matrix evaporation was

Table 1
Recovery of analytes after in situ matrix evaporation and LODs ($n = 5$)

Ion	Added (ng)	Matrix					LOD (ng/l)
		HF (40%)[a]	HCl (30%)[a]	HNO_3 (69%)[b]	H_2O_2 (30%)[b]		
		Recovery (%)	Recovery (%)	Recovery (%)	Added (μg)	Recovery (%)	
SO_4^{2-}	1000	99 ± 1	98 ± 1	105 ± 5	100	99 ± 5	20
PO_4^{3-}	1000	98 ± 1	92 ± 1	99 ± 2	100	98 ± 2	75
NH_4^+	1000, 100[c]	104 ± 4	104 ± 4	105 ± 5	100	102 ± 2	120
Li^+	20	95 ± 5	105 ± 10	95 ± 5	0.5	96 ± 2	6
Na^+	100, 1000[c]	86 ± 3	98 ± 5	86 ± 2	100	110 ± 5	130
K^+	100, 1000[c]	108 ± 5	85 ± 2	98 ± 1	5	96 ± 2	60
Mg^{2+}	100, 1000[c]	105 ± 6	95 ± 3	99 ± 1	5	98 ± 2	110
Ca^{2+}	100, 1000[c]	98 ± 2	93 ± 2	102 ± 1	10	99 ± 2	110

[a] Suprapur grade (E. Merck, Germany).
[b] AR grade (E. Merck, India).
[c] In HNO_3 matrix. Sample size and preconcentration/dilution for cations: (1) HF (20 → 0.5 ml), (2) HCl (10 → 0.5 ml), (3) HNO_3 (2 → 1 ml), (4) H_2O_2 (10 → 40 ml). For anions: (1) HF (25 → 1.0 ml), (2) HCl (25 → 0.5 ml), (3) HNO_3 (2 → 1 ml), (4) H_2O_2 (1 → 20 ml). Recovery was calculated after correcting the sample values, which are given in Table 2. The LOD values listed above are divided by a concentration factor 10 for all the analytes. Injection volume for cations, 25 μl, for anions, 100 μl.

Table 2
Trace ion concentrations ($\mu g\,l^{-1} \pm \sigma$) determined by suppressed IC ($n = 3$) and manufacturer's specifications (M)

Matrix	Method	SO_4^{2-}	PO_4^{3-}	NH_4^+	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
HCl[a]	IC	15 ± 1	23 ± 2	0.07 ± 0.005[c]	<0.01	7 ± 1	4 ± 1	3 ± 1	14 ± 1
	M	<100	<10	<0.5[c]	<1	<20	<10	<5	<30
HF[a]	IC	73 ± 7	84 ± 10	0.04 ± 0.005[c]	<0.01	9 ± 1	8 ± 1	6 ± 1	15 ± 1
	M	<100	<100	n.a.	<1	<10	<10	<5	<10
HNO_3[b]	IC	1.18 ± 0.11[c]	0.68 ± 0.12[c]	0.05 ± 0.006	<0.1	0.34 ± 0.01[c]	0.32 ± 0.01[c]	0.05 ± 0.004[c]	0.20 ± 0.01[c]
	M	<1[c]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	<1[c]
H_2O_2[b]	IC	77 ± 3[c]	35 ± 1[c]	19 ± 1[c]	<1.0	23 ± 2[c]	0.93 ± 0.05[c]	0.31 ± 0.01[c]	0.83 ± 0.02[c]
	M	<500[c]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a

[a] Suprapur grade (E. Merck, Germany).
[b] AR grade (E. Merck, India).
[c] Values in $\mu g\,ml^{-1}$. Sample size and preconcentration/dilution for cations: (1) HF (20 → 0.5 ml), (2) HCl (10 → 0.5 ml), (3) HNO_3 (2 → 1 ml), (4) H_2O_2 (10 → 40 ml). For anions: (1) HF (25 → 1.0 ml), (2) HCl (25 → 0.5 ml), (3) HNO_3 (2 → 1 ml), (4) H_2O_2 (1 → 20 ml). Injection volume for cations, 25 μl, for anions, 100 μl, n.a.: not available.

carried on a water bath no such problem was observed. However, in the case of HF less recovery of sulfate and phosphate (∼85%) was observed. Therefore, after the first distillation the residues were treated with 0.5 ml of nitric acid (suprapur) and the second distillation was carried out. In this case recoveries of sulfate and phosphate were 98 ± 1 (%) and 99 ± 1(%), respectively. Improved recoveries may be due to decomposition of fluorocomplexes by nitric acid treatment [22]. The residual amount of nitrate left in HF matrix did not interfere with the chromatographic separation and detection of sulfate and phosphate.

3.4. Sample analysis, accuracy and precision

The proposed matrix evaporation procedure was applied for the determination of trace ions in a variety of matrices [HCl, HF (both suprapur grade), HNO_3 and H_2O_2 (AR grade)] and the chromatograms of anions in HCl and process blank are presented in Fig. 2. The preconcentration factors (2–50) required for each matrix depends on the level of impurities present in the reagents are given in Tables 1 and 2. Since the level of impurities is high in H_2O_2, dilution was carried out prior to analysis depending on the analyte concentration. Quantification of analytes was carried out from an external calibration curve which was linear ($R^2 > 0.991$) in concentrations ranging from 0.1 to 1.0 mg/l (anions) and between 0.01 and 1.0 mg/l (cations). The accuracy of this method was evaluated on the basis of recovery data (Table 1) and by comparing the impurity levels found by this procedure with that specified by the manufacturer (Table 2). The values obtained by the proposed method are found to be in good agreement with the manufacturer specification.

3.5. Advantages and disadvantages

The main advantages of this in situ low temperature evaporation system are achievement of clean environment for the analyte and the analyst, common digestion procedure for a variety of matrices, provides quantitative recovery of phosphate and sulfate, simple experimental set up, does not require any costly reaction vessels and heating accessory, unattended operation for a large number of samples at a time (for the laboratory which analyses routine or occasionally). The disadvantages are not applicable for high boiling reagents (acid/solvent) and not suitable for analysing fluoride, chloride and nitrate. Though sample preparation time is long, it can be considerably reduced (when analyzing many samples) by digesting multiple samples simultaneously on a water bath.

4. Conclusion

Solubility of various acids in glycerol due to hydrogen bonding has been utilized for the development of in situ evaporation system. The proposed method successfully overcomes the two major disadvantages of conventional open evaporation system by preventing the analyte contamination from the normal laboratory environment and the contamination of clean laboratory during the matrix evaporation. Other than cost effectiveness, its applicability to a large number of matrices for the analysis of most of ionic impurities with extremely low process blank and free from dehydration problem proves to be one of the most useful procedure for any laboratory.

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