

Analysis of sub-boil distilled water, hydrochloric and nitric acid for trace element impurities by ICP-MS

V Balaram*, K Chandrasekhar¹, A K Agrawal², P N Sharma¹,
Sunita Ganju², T.Nageswara Rao¹, K.V.Anjaiah,
Sajid Husain¹ & Krishan Lal²
National Geophysical Research Institute,
Hyderabad 500 007, India

Received 21 June 1999; revised 21 March 2000

A method has been designed for the precise estimation of a few trace and ultra-trace elements in high purity sub-boil distilled water and hydrochloric and nitric acids using inductively coupled plasma mass spectrometers of two different makes. The trace element concentrations of majority of the elements analysed in sub-boil distilled water are found to be below detection limits. A comparison of the trace element impurity levels obtained in hydrochloric and nitric acids with the maximum allowable impurity levels for high purity reagents documented in SEMI, suggests that these purity levels confirm with the specifications given for the high pure reagents.

The quality of acids and other chemical reagents is of paramount importance when dealing with the analysis of high purity materials and working at ng/ml (ppb) and sub-ppb concentration levels¹. These studies require rigorous control over the laboratory environment and improved methods of characterizing trace element impurities in high pure reagents and acids. The purpose of this work is to provide a method for the assessment of the quality of ultrapure water and acids used in such studies by means of inductively coupled plasma mass spectrometry (ICP-MS). In this work, a few trace and ultra-trace elements are determined in sub-boil distilled water, hydrochloric and nitric acids using two ICP-MS instruments of different makes, deployed at two different institutions. The concentrations of the trace elemental impurities in the two acids are compared with the documented maximum limits of impurities specified for the semiconductor industry.

Experimental

The ICP-MS instruments PlasmaQuad PQ1 (VG Elemental, UK) at NGRI and UltraMass 700 (Varian Australia Pvt. Ltd. Australia) at IICT are used.

The containers used throughout the study were cleaned using the procedure described by Creed and co-workers². The containers were filled with 18 mega ohms water and acidified so that the solution contained 1% HNO₃ and HCl. The containers were allowed to stand overnight. Next day the 1% HNO₃/HCl solution was poured out and the container was rinsed five times with 18 mega ohms water and allowed to dry in a clean environment.

The preparation procedure of ultra high purity water, hydrochloric and nitric acids is described in detail by Gupta and co-workers³. These high purity materials were stored in polyethylene bottles having screw caps with built-in-washers.

ICP-MS analysis

The isotopes chosen were free of interferences wherever possible. Same analyte isotopes were used by both laboratories. The operating conditions were optimized to have minimum oxide, hydroxide and doubly-charged interference effects on the analyte isotopes. In order to compensate for signal drift due to changes in nebuliser efficiency, gradual clogging of the torch and interface, matrix induced suppressions and enhancement effects, and for minimising mass discrimination and space-charge effects, ¹⁰³Rh was used as an internal standard in all these investigations. Data acquisition was done in the mass scanning mode. NIST 1643b and NIST 1643c were used for calibration and also as control samples⁴. While the analysis work was carried out in routine analytical laboratories every effort was made to avoid contamination.

Results and discussion

When the chemical analysis of elements present at ultra-trace levels (less than 1 µg/ml) is being carried out, stability of the reagents is a major factor. The stability of these reagents depends on a number of factors, such as pH, type of sample matrix and the contamination associated with the container. Since the containers were thoroughly washed and cleaned before storing these reagents, contamination associated with the containers is expected to be at the minimum level. In the case of nitric and hydrochloric acids, blank subtraction was done using

¹ Indian Institute of Chemical Technology, Hyderabad 500 007, India

² National Physical Laboratory, New Delhi 110 012, India

Table 1 - Concentrations of some trace elements in sub-boil distilled water, sub-boil distilled hydrochloric and nitric acids

Element	Sub-boil distilled water (ng/ml)		Sub-boil distilled hydrochloric acid (ng/ml)			Sub-boil distilled nitric acid (ng/ml)		
	NGRI ¹	IICT ²	NGRI ¹	IICT ²	SEMI ³ (µg/ml)	NGRI ¹	IICT ²	SEMI ³ (µg/ml)
Be	<0.01	<0.01	<0.01	0.01	-	<0.01	ND	-
B	2.88	3.84	2.65	1.23	0.1	10.68	0.29	1
V	-	0.02	-	ND	-	4.96	9.81	-
Cr	0.10	0.07	8.30	7.02	1	54.55	0.89	0.1
Mn	<0.01	-	<0.01	-	1	27.22	-	0.5
Fe	<0.01	-	<0.01	-	0.2	66.01	-	0.2
Co	<0.01	<0.01	<0.01	0.02	0.1	0.64	4.39	0.5
Ni	<0.02	-	<0.02	-	0.1	<0.02	-	0.05
Cu	<0.02	<0.01	13.15	19.04	0.1	75.60	3.80	0.05
Zn	<0.02	-	<0.02	-	1	0.60	-	1
As	-	<0.01	2.31 [#]	12.57	-	7.38	9.37	-
Se	0.25	<0.30	<0.01	ND	-	6.61	ND	-
Rb	0.01	<0.01	<0.01	0.01	-	0.05	0.01	-
Sr	<0.01	-	<0.02	-	1	<0.01	-	1
Mo	0.56	0.22	<0.01	0.44	-	8.27	0.66	-
Ag	0.49	<0.01	0.88	0.22	0.1	0.18	4.35	0.5
Cd	<0.01	<0.01	<0.01	0.41	1	0.11	17.46	0.5
Sb	<0.01	<0.01	<0.01	ND	-	0.11	ND	-
Ba	<0.01	<0.01	0.07	4.88	1	<0.01	1.57	1
Tl	0.04	<0.01	0.04	0.02	-	0.03	0.06	-
Pb	0.04	0.02	0.05	1.26	-	0.55	8.04	-
Bi	<0.01	<0.01	0.13	0.03	-	1.39	0.03	-

¹PlasmaQuad PQ1

- not available

²UltraMass 700

ND = not detected

³ SEMI= Semiconductor Equipment Manufactures Institute (SEMI)

Specifications for reagents CI STD 21-85

Measurement precision <5% RSD in both cases

As was determined by GF-AAS with Zeeman background correction facility⁶

high purity sub-boil distilled water, and for the analysis of high purity sub-boil distilled water, counts obtained from dry-plasma for the respective analytes were used for background subtraction for all the analyte masses associated with both the standards and samples. The data of trace element impurities obtained in high pure sub-boil distilled water, hydrochloric and nitric acid are presented in Table 1. Results obtained on sub-boil distilled water suggest that for almost all the elements, the estimations have been carried out at their respective detection limits. In addition, the values obtained for different elements by both the instruments show a reasonable agreement.

In the case of ultra-pure acids, the maximum permissible impurity levels for high purity reagents are documented in the SEMI specification document⁵. Using conventional nebulisation techniques such as the one used in the present investigation, it is possible to directly aspirate some aggressive reagents, such as nitric and

hydrochloric acids for a short duration without any damage to the sampler or skimmer cones of the plasma interface. Trace element concentrations detected in two high pure acids by both the instruments are presented in comparison with maximum permissible impurity levels for high purity reagents (SEMI). There is a reasonable agreement in the results of the trace element impurities in hydrochloric acid obtained by both the instruments. The accurate estimation of As(I) in hydrochloric acid is difficult by ICP-MS because of the direct overlapping interference of ⁴⁰Ar³⁵Cl⁺ on ⁷⁵As⁺. Arsenic is a monoisotopic element and there is no alternate isotope available for use. Hence, arsenic in hydrochloric acid was estimated using graphite furnace atomic absorption spectrometry (GF-AAS) with Zeeman background correction facility (ZBGC)⁶. The concentration levels of the impurities are much lower than the maximum permissible levels in high purity reagents.

Table 2 - Concentrations of various trace elements (ng/ml) in NIST 1643b & 1643c, (water reference samples), obtained by both instruments in the present investigation in comparison with certified values

Element	NIST 1643b			NIST 1643c		
	ICP-MS ¹	ICP-MS ²	Cert. ³ values	ICP-MS ¹	ICP-MS ²	Cert. ⁴ values
Be	19.61±0.61	19.55±0.88	19±1.88	23.01±0.92	23.33 ±1.12	23.2 ±2.2
B	93.33±2.01	94.11±3.41	94 ±3.2	120.1±2.40	118.07± 3.07	119.0 ±1.4
V	42.72 ±1.27	44.00±1.81	45.2±2.1	30.5 ±0.92	30.80±1.41	31.4±2.8
Cr	19.27±0.53	19.34±0.86	18.6±0.70	20.11±0.50	19.50±0.60	19.00±0.6
Mn	27.03±1.08	27.59±1.17	28.0±2.1	34.33 ± 1.03	36.14±1.51	35.1±2.2
Fe	103.06±4.54	102.47±5.10	99±3.3	108.3 ± 4.87	108.55±5.43	106.1±3.0
Co	25.72±0.86	25.47±0.82	26±0.9	23.70 ± 0.36	23.63±0.57	23.50±0.8
Ni	48.71±1.20	48.50±1.82	49±1.9	61.20 ± 3.06	61.30±3.10	60.60±7.3
Cu	21.03±0.87	22.61±0.86	21.9±0.8	21.30 ± 0.75	21.71±1.07	22.30±2.8
Zn	65.12±2.33	64.79±2.47	66±2.5	74.25 ± 2.97	74.57±3.2	73.90±0.9
As	48.07±1.27	50.13±1.30	49±1.4	82.15 ± 2.05	83.70±2.5	82.10±1.2
Se	9.26±0.32	9.2±0.30	9.7±0.3	12.51 ± 0.56	12.32±0.6	12.70±0.7
Rb	ND	ND	-	11.75 ± 0.05	11.22±0.2	11.40±0.2
Sr	227.77±3.19	220.70±4.52	227±6.0	270.70±2.43	271.09±5.1	263.60±2.6
Mo	83.64±4.05	82.88±4.10	85±3.7	107.81± 5.17	106.66±2.33	104.30±1.9
Ag	10.01±0.39	10.21±0.51	9.8±0.70	2.11± 0.04	2.10±0.10	2.21±0.30
Cd	19.38±0.80	20.78±0.81	20±1.0	12.50± 0.19	12.35±0.60	12.20±1.0
Ba	44.49±0.86	45.91±0.90	44±1.1	50.10± 0.50	50.25±0.70	49.60±3.1
Tl	8.21±0.37	8.41±0.41	8±0.50	7.89± 0.18	8.02±0.20	7.90*
Pb	24.11±1.20	25.09±1.10	23.7±2.1	37.44± 1.42	36.19±1.6	35.30±0.9
Bi	11.30±0.51	11.32±0.46	11±0.50	12.33± 0.44	12.18±0.54	12.00*

¹Plasma Quad PQ1²Ultra Mass 700³National Institute of Standards and Technology, Certificate of Standard Reference Material 1643b, Trace Elements in Water, 1984⁴National Institute of Standards and Technology, Certificate of Standard Reference Material 1643c, Trace Elements in Water, 1991

*average of three estimations, Precision <5% RSD in both cases

*Information values only

Accuracy and precision of analysis

During the analysis of analytes present at extremely low levels, systematic error in the analysis will increase with decreasing concentration⁷. To ensure adequate precision, average values of the results of three dependent determinations are shown for each element. The assessment of the accuracy of the analytical method adopted here is a problem especially, when dealing with a suite of elements, such as the one under consideration. Since these high purity materials were not analysed before, no data is available for comparison. To assess the accuracy of the procedure, NIST 1643b and 1643c (Trace Elements in Water Reference Samples from National Institute of Standards and Technology, USA) were analysed along with the samples as unknown samples. The results obtained in this study for NIST 1643b and NIST 1643c are presented in comparison with certified data (Table 2). The overall agreement is reasonably good with precisions showing <5% RSD with a comparable accuracy in most cases. However,

agreement between the results obtained by both instruments for elements such as, Mo, Ag, Cd, Ba and Pb is not good (Table 1). The suppression and enhancement effects of the acid matrix on the analyte signal depends upon the design of the instrument. As the calibration standards do not contain acid matrix, variations are expected in the results obtained by both instruments especially when the analysis was carried at very low levels. In addition, contribution from sample contamination cannot be ruled out as both sample preparation and analysis were not carried out under clean-room conditions.

Conclusion

The high sensitivity and versatility of ICP-MS technique makes it uniquely suited to the trace analysis of ultra-high purity materials, such as sub-boil distilled water, hydrochloric and nitric acids. The reasonable agreement between the results produced by the two ICP-MS instruments of different make at two different institutions

reveals that the overall ICP-MS methodology including the calibration procedure is well suited for the estimation of trace element impurities in high purity materials. The concentrations of trace element impurities in the high purity materials analysed suggest that those levels are much lower than the maximum permissible impurity levels in these substances. The sub-boil distilled water, hydrochloric and nitric acids can be used in making standard reference materials for Certification Programs.

References

1. Broekaert J.A C & Tolg G *Mikrochim Acta*, (1990), II, 173.
2. Creed J T, Martin T D & Sivaganesan M *JAWWA*, February, (1995), 104.
3. Gupta P.K, Chetna K, Sunita G, Agrawal, A.K Ramachandran R, Sarkar A K & Krishan Lal, *Fr. J Anal. Chem.*, (1993), 345, 278.
4. Balaram V, *Atom. Spectrosc.* (1993), 14, 174.
5. Semiconductor Equipment Manufacturers Institute (SEMI) Specification for reagents CI STD 21-85.
6. Balaram V, Sunder Raju P V, Ramesh S L, Anjaiah K V, Dasaram B, Manikyamba C, Ram Mohan M & Sarma D.S. *Atom. Spectrosc.*, 20 (1999), 155.
7. Tolg G. *The role of trace elements for life from the point of view of an analytical chemist. From metal compounds in environment and life*, edited by E. Merian and W. Haerdi (*Science and Technology Letters*, UK) 1992 pp. 1-22.