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DETERMINATION OF TRACE IMPURITIES IN HIGH PURITY WATER BY EMISSION SPECTROSCOPY AND FLAME PHOTOMETRY

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ABSTRACT

A spectrochemical method for the determination of trace amounts of Fe, Mg, Mn, Sn, Cr, Bi, Ni, Ca, Na, Zn, Sr, Al, Ba and Cu in high purity water is described. In addition Na, Li and K are measured by flame photometry.

The standards used in the spectrochemical method are prepared by evaporation in hot plate of 50 mL standard solution in Teflon beaker to dryness, the residue being dissolved with 500 μ L hot HCl (1:1). Four hundred μ L of this solution is evaporated under infra-red lamp on Apiezon treated flat top graphite electrodes. The residue is submitted to a direct current arc excitation.

The accuracy is estimated by the spectrochemical method with a direct procedure sample preparation. The relative standard deviation varies from $\pm 4\%$ to $\pm 27\%$.

For the elements Na, Li and K standard solutions are concentrated fiftyfold by a simple evaporation procedure and then measured by flame photometry. The standard deviation and accuracy are given.

DETERMINAÇÃO DE IMPUREZAS AO NÍVEL DE TRAÇOS EM ÁGUA DE ALTA PUREZA POR ESPECTROGRAFIA DE EMISSÃO E FOTOMETRIA DE CHAMA

RESUMO

Descreve-se um método espectrográfico para determinação de elementos ao nível de traços em água de alta pureza. As impurezas determinadas são: Fe, Mg, Mn, Sn, Cr, Bi, Ni, Ca, Na, Zn, Sr, Al, Ba e Cu. Os elementos Na, Li e K são determinados por fotometria de chama.

Para a determinação espectrográfica obtêm-se a série de amostras de referência pela evaporação de 50mL de solução padrão em béquer de Teflon numa chapa aquecedora. O resíduo resultante é dissolvido a quente com 500 μ L de HCl (1:1). Quatrocentos μ L dessa solução são depositados sobre um eletrodo de grafita de superfície plana tratado com Apiezon e secos em lâmpada infra-vermelha. O resíduo é excitado em um arco de corrente contínua.

A exatidão é estimada pelo próprio método espectrográfico, onde as amostras de referência são preparadas de uma forma direta. O desvio padrão relativo varia de 4 a 27%.

Para determinação de Na, Li e K as soluções de referência são concentradas 50 vezes por meio de evaporação em chapa aquecedora e, então, medidas no fotômetro de chama. Apresentam-se o desvio padrão relativo e a exatidão.

INTRODUCTION

A method which would permit the quantitative determination of a large number of elements in trace amounts in high purity water is emission spectroscopy.

There are many papers in literature that describe methods which determine impurities in natural water. Khitov and Belovsov⁽¹⁾ use "rotating-disc-electrode" method to analyse natural waters with mineral contents for 10 microelements without preliminary concentration. Silvey and Brennan⁽³⁾ determined 17 minor elements in natural water by concentration traces using chelating reagents 8-quinolinol, tannic acid and thionalide. A determination of 12 impurities in high purity water was suggested by Ko⁽²⁾ where the sample is concentrated by evaporation with In as the internal standard. The residue is analysed by a graphite spark technique using flat top electrodes. The present paper describes a modification of the Ko⁽²⁾ methods involving some different impurities, dc arc technique and without the use of internal standard.

Flame photometry was the other technique used in this paper to analyse three other impurity elements.

EXPERIMENTAL

PART I – SPECTROGRAPHIC ANALYSIS

Preparations of Standard Solutions

Standard solutions are obtained by dissolutions of specpure chemical compounds of the corresponding elements from Johnson Matthey and Co. Initially, a concentrated solution containing 0.1% of each impurity was prepared, the other solutions, more diluted, are obtained by successive dilution of the 0.1% standard solution, with bidistilled water until the desired concentration is reached.

Method one

Aliquots of standard solutions are deposited, with micropipetting system, directly on Apiezon treated flat top graphite electrodes. After dried under infra-red lamp, the resultant residue is the same as obtained by method two. This is done for all electrodes that compose the series of standard solutions, i.e., 1.0 to 0.001 $\mu\text{g}/\text{mL}$. Four standard solution series obtained by this procedure are excited under experimental conditions mentioned in Table I. Concentration range determination reached by working curve standards are given in Table II.

Method two

A series of ten standard solutions from 1.0 to 0.001 $\mu\text{g}/\text{mL}$ are obtained by successive dilution of 0.1% standard solution. Evaporate in hot plate 50 mL each standard solution in 50 mL Teflon becker until dryness, dissolve the residue with 500 μL hot HCl (1:1). Add one drop Apiezon solution on top of each electrode before adding sample. Deposit on electrode 400 μL of the standard prepared and dry under infra-red lamp. That is done in triplicate for all standards. Expose on spectrograph under experimental conditions in Table I. Concentration range determination reached by working curve standards are shown in Table II.

Tabela I

Experimental Conditions and Equipment

SPECTROGRAPH	Jarrel Ash 3.4 m Ebert Mount grating spectrograph set in wavelength range 220-340 nm. Grating: 590 lines/mm having a reciprocal linear dispersion of 0.247 nm/nm in the second order.
EXCITATION SOURCE	DC arc from Jarrell Ash Standard Varisource
SLIT WIDTH	10 μ
PREBURN	0 sec
EXPOSURE TIME	30 sec
ELECTRODES	Anode - AGKSP L 3809 (6.15 mm diameter graphite rod) of Union Carbide Corporation Cathode - AGKSP L 3803 (3.05 mm diameter graphite rod) of Union Carbide Corporation
CURRENTS	10 A
ARC GAP	4 mm
PHOTOGRAPHIC PROCESSING	Plates are developed for 3 minutes at 18°C using Kodak D-19 developer, fixed in Kodak F-5 fixer, washed and dried.
PHOTOGRAPHIC PLATES	Kodak Spectrum Analysis n ^o 1
DENSITOMETER	Jarrell Ash comparator microphotometer

Table II

Spectrochemical Method. Analytical Lines and Estimation Range Obtained By Method one and two. Relative Standard Deviation According to Method one

ELEMENT	ANALYTICAL LINE (nm)	ESTIMATION RANGE $\mu\text{g/mL}$		RELATIVE STANDARD DEVIATION (%)
		Method 1	Method 2	
Fe	259.84	0.002 - 1.0	0.005 - 0.5	9.7
Mg	277.98	0.003 - 0.2	0.01 - 0.5	6.0
	277.67	0.007 - 1.0	0.007 - 1.0	
Mn	279.83	0.0025 - 0.2	0.004 - 1.0	18.1
	305.44	0.0065 - 1.0	-	
Sn	284.00	0.002 - 1.0	0.001 - 0.5	10.3
Cr	284.33	0.0015 - 0.2	0.005 - 0.5	10.8
	265.36	0.01 - 1.0	0.02 - 1.0	
Bi	306.77	0.01 - 0.5	0.02 - 1.0	13.3
Ni	305.08	0.002 - 1.0	0.005 - 1.0	10.1
Ca	315.89	0.005 - 0.2	0.01 - 0.2	8.5
Na	330.30	0.04 - 1.0	0.05 - 1.0	23.3
Zr	334.50	0.01 - 1.0	0.05 - 1.0	11.4
Sr	460.73	0.01 - 0.1	0.05 - 1.0	26.7
Al	308.22	0.0015 - 0.2	-	16.7
	265.25	0.01 - 1.0	0.01 - 1.0	
Ba	233.53	0.01 - 1.0	0.002 - 1.0	12.9
Cu	327.40	0.001 - 0.05	0.002 - 0.2	3.9
	282.44	0.001 - 1.0	0.1 - 1.0	

PRECISION

To check relative standard deviation of the spectrographic method 18 electrodes prepared according to method one are excited. Two different concentrations, 0.05 and 0.2 $\mu\text{g}/\text{mL}$, were taken into account depending on the element and its estimation range. The relative standard deviation values for different elements are listed in Table II.

ACCURACY

Triplicate fifty milliliter aliquots of each of the standard samples 0.05 and 0.5 $\mu\text{g}/\text{mL}$ are evaporated in Teflon beakers on hot plate to dryness. The residues are dissolved with 500 μL hot HCl (1:1). Four hundred μL of these solutions are evaporated on top of each graphite electrode, following the same procedure of method two. The electrodes are submitted to spectrographic analysis and the concentrations of the elements are estimated from the analytical curves obtained by the methods one and two. Results are given in Table III.

PART II – DETERMINATION OF Na, Li AND K BY FLAME PHOTOMETRY

Micronal flame photometer, B-262 model is used to determine the elements Na, Li and K.

Concentration as low as 1 $\mu\text{g}/\text{mL}$ for sodium, 0.1 $\mu\text{g}/\text{mL}$ for potassium and 0.1 $\mu\text{g}/\text{mL}$ for lithium can be measured directly with the flame photometer. The purpose of this work, nevertheless, is the detection of lower limits. Thus, standard and sample solutions are concentrated fiftyfold in fused quartz beakers.

Five hundred mL of solution, containing known amounts of Na, Li and K, are concentrated in hot plate to ten mL. The photometric measurements are done with ten standard solutions prepared according to this procedure. The relative standard deviations are shown in Table IV.

The accuracy of the method is indicated by the relative error as a percentage of the assumed true result (Table IV).

DISCUSSION

High purity water can be submitted to spectrochemical analysis under direct current arc excitation after a simple evaporation enrichment procedure. If necessary, the estimation range may be altered by varying the enrichment factor.

The precision of the spectrochemical method is shown in Table II and the relative standard deviation ranges approximately from ± 4 to $\pm 27\%$ depending on the element.

The direct use of synthetic standards, excluding chemical preparation as it is done for the samples, is a current practice in spectrochemical analysis but it may result in a poor accuracy. Therefore, depending on the standardization method, the accuracy may be too low as it can be seen in method one (Table III). For this reason, method two is the recommended practice for the standardization procedure.

As can be seen from Table III, the relative error is high for some elements, mainly in the 0.5 $\mu\text{g}/\text{mL}$ concentration range. In such a case it is suggested to use spectrographic method only to do a semi-quantitative analysis, and the spectrum can also be used as a visual estimate for the relative concentration. On the other hand, this procedure is very simple, as it permits a multielementar analysis and estimates the concentration of the impurities present in water samples.

Table III

Accuracy of the Spectrochemical Method

ELEMENT	ANALYTICAL LINE (nm)	ADDED ($\mu\text{g/mL}$)	METHOD ONE		METHOD TWO	
			FOUND ($\mu\text{g/mL}$)	RELATIVE ERROR (%)	FOUND ($\mu\text{g/mL}$)	RELATIVE ERROR (%)
Fe	259.84	0.5	0.052	90	0.26	48
		0.05	0.022	56	0.052	4
Mg	277.98	0.5	0.18	64	0.38	24
		0.05	0.030	40	0.043	14
	277.67	0.5	0.21	58	0.34	32
		0.05	0.039	22	0.044	12
Mn	279.83	0.5	0.57	14	0.74	48
		0.05	0.03	40	0.041	18
	305.44	0.5	0.19	62	—	—
		0.05	0.042	16	—	—
Sn	284.00	0.5	0.08	84	0.47	6
		0.05	0.008	84	0.052	8
Cr	284.33	0.5	0.08	84	0.17	66
		0.05	0.020	60	0.037	26
	265.36	0.5	0.12	76	0.21	56
		0.05	0.030	40	0.048	4
Bi	306.77	0.5	0.08	84	0.6	20
		0.05	0.09	82	< 0.02	—
Ni	305.08	0.5	0.15	70	0.24	52
		0.05	0.035	30	0.053	6
Ca	315.89	0.5	0.3	40	> 0.2	—
		0.05	0.045	10	0.035	10
Na	330.30	0.5	0.39	22	0.42	16
		0.05	0.083	66	0.067	34
Zn	334.50	0.5	0.31	48	0.5	0
		0.05	0.029	42	0.053	6
Sr	460.73	0.5	0.47	6	0.33	34
		0.05	0.043	14	0.045	10
Al	308.22	0.5	> 0.2	—	—	—
		0.05	0.033	34	—	—
	265.25	0.5	0.29	42	0.36	28
		0.05	0.041	18	0.047	6
Ba	233.53	0.5	0.27	46	0.67	34
		0.05	0.028	44	0.045	10
Cu	327.40	0.5	—	—	—	—
		0.05	0.06	20	0.052	4
	282.44	0.5	0.24	52	0.44	12
		0.05	0.046	8	0.098	96

Table IV

Precision and Accuracy of the Flame Photometric Method

STANDARD SOLUTION	ELEMENT	ADDED ($\mu\text{g/mL}$)	FOUND ($\mu\text{g/mL}$)	RELATIVE STANDARD DEVIATION (%)	RELATIVE ERROR (%)
I	Na	0.4	0.43	4	8
	K	0.02	0.018	30	10
	Li	0.02	0.02	9	0
II	Na	0.02	0.033	19	65
	K	0.002	0.002	81	0
	Li	0.002	0.002	0	0

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