



**DETERMINATION OF CHLORINE AND COPPER IN HIGH  
PURITY WATER BY RADIOACTIVATION ANALYSIS**

by

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Summary

This work outlines a radioactivation procedure for quantitative determination of chlorine and copper in parts per billion (ppb) level, in high purity water.

Water samples (100 ml.) in polyethylene containers are irradiated during 35 minutes in a  $10^{13}$  n/sec.  $\text{cm}^2$  thermal neutron flux. After a 10 minutes cooling time, carriers for iron, chlorine and copper are added and the hydroxides precipitated by addition of sodium hydroxide. Chlorine is precipitated in the filtrate as silver chloride, the precipitate separated on a sintered glass plate and the induced Cl-38 (37.3 minutes half-life, beta of 4.8 Mev) is beta counted with a G.M. tube using an aluminum absorber to cut eventually extraneous beta contamination.

The iron and copper hydroxides are dissolved with hydrochloric acid and the iron is precipitated again with  $\text{NH}_3$  gas. The iron hydroxide is centrifuged and discarded. The supernatant is acidified and the copper precipitated as sulfide. The precipitate is mounted and gamma-counted, its activity measured by the height of the Cu-64 (0.510 Mev, 12.8 hours half-life) photo-peak, using a single pulse height analyser.

The amount of chlorine and copper is calculated by comparison with the activities of standards using the "internal standard" method.

The procedure suggested in this work possibilites the determination of amounts of chlorine and copper as low as 0.05 ug.

## ANALYSE PAR ACTIVATION DE CHLORE ET DE CUIVRE EN

### EAU DE HAUTE PURETÉ

#### Résumé

Les auteurs décrivent une méthode pour la détermination de chlore et de cuivre à l'aide de l'analyse par activation, aux niveaux de parties par billion, en eau de haute pureté.

On irradie des échantillons de 100 ml. d'eau dans des récipients de polythène pendant 35 minutes, dans un flux de neutrons lents d'environ  $10^{13}$  n/cm<sup>2</sup>.s. Après un refroidissement de 10 minutes, on introduit dans les échantillons, des entraîneurs de fer, de chlore et de cuivre, et ensuite on précipite les hydroxydes de fer et de cuivre avec une solution d'hydroxyde de sodium. Dans le filtré on précipite le chlore sous la forme de chlorure d'argent, on filtre en plaques spéciales et on mesure l'activité du chlore-38 (37,3 minutes de demi-période, rayonnement bêta de 4,8 Mev) au compteur Geiger, avec absorbeur d'aluminium pour éliminer quelque impureté qui pourrait contaminer le chlore-38.

On dissout les hydroxydes de fer et de cuivre avec l'acide chloridrique, et on précipite de nouveau le fer avec le gas ammoniacque. On centrifuge l'hydroxyde de fer et on le rejette ensuite. Le liquide surnageant est acidulé et on précipite le

sulfure de cuivre. On monte le précipité et l'activité du cuivre-64 (0,510 Mev, demi-période de 12.8 heures) est mesurée au spectromètre à rayons gamma.

Les quantités de chlore et de cuivre sont calculées par comparaison avec des étalons traités dans les mêmes conditions que les échantillons, en se servant de la méthode de l'étalon interne.

Par cette méthode on a déterminé des quantités de chlore et de cuivre jusqu'à 0,05 microgrammes.

### ANÁLISE POR ATIVAÇÃO DE CLORO E COBRE EM ÁGUA DE ELEVADA PUREZA

por

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#### Resumo

Neste trabalho os autôres descrevem um processo para a determinação quantitativa de cloro e cobre, aos níveis de partes por bilhão, em água de elevada pureza, por meio de análise por ativação.

Amostras de 100 ml de água são irradiadas em frascos de polietileno durante 35 minutos em fluxo de neutrons térmicos ao redor de  $10^{13}$  n/seg.cm<sup>2</sup>. Após um período de resfriamento, adicionam-se às amostras carregadores de ferro, cloro e cobre, precipitando-se em seguida os hidróxidos de ferro e cobre mediante a adição de uma solução de hidróxido de sódio. No filtrado precipi-

ta-se o cloro sob a forma de cloreto de prata, filtra-se em placas especiais e determina-se a atividade do Cl-38 (37,3 minutos de meia-vida, beta menos de 4,8 Mev), em um Geiger usando absorvedor de alumínio para eliminar partículas beta de alguma impureza que eventualmente permanecesse contaminando o Cl-38.

O precipitado contendo os hidróxidos de ferro e cobre é dissolvido com ácido clorídrico, reprecipitando-se o ferro com amoníaco gasoso. Separa-se o hidróxido de ferro por centrifugação desprezando-se o mesmo em seguida. Acidula-se o sobrenadante e o cobre é precipitado sob a forma de sulfeto. O precipitado é montado e sua atividade determinada pela altura do pico do isótopo de Cu-64 (0,510 Mev, 12,8 horas de meia-vida) num gama espectrômetro.

As quantidades de cloro e cobre são calculadas por comparação com a de padrões tratados nas mesmas condições das amostras, usando-se o processo do padrão interno. Dêste modo pode-se dosar até 0,05 ug de cloro e cobre.

## INTRODUCTION

The scope of this paper is to establish a fast and precise method for the simultaneous determination of chlorine and copper in high purity water, as is the case of water used as moderator in nuclear reactors.

Chlorine and copper even at a very low concentration, specially when found simultaneously in water, are dangerous corrosion agents for aluminum. As it is well known, aluminum is a metal widely used in swimming-pool reactor as fuel element clad or as structural element. Therefore it is profitable a rigorous control of both elements in water.

As the concentration of chlorine and copper in high purity water is very low, the classical methods of analysis are not sensible enough for determining those elements. To overcome this difficulty the activation analysis technique is used. The radioactivation sensitivity is high enough to allow the determination of 0.5 ppb of each element.

## Procedure.

### 1. Reagents

- a. Fe-III carrier solution:  $\text{Fe}_2(\text{SO}_4)_3$  - 10mg.Fe/ml.
- b. Cl carrier solution: NaCl, 10 mg.Cl/ml
- c. Cu carrier solution:  $\text{Cu}(\text{NO}_3)_2$ , 10 mg.Cu/ml
- d. Silver nitrate solution: 100 mg.Ag/ml
- e. 70% Nitric Acid
- f. 12M. Hydrochloric Acid
- g. 10% Sodium hydroxide solution
- h.  $\text{NH}_3$  gas
- i.  $\text{H}_2\text{S}$  gas



## Counting Equipment

Radiochlorine (silver chloride) is beta counted using a Geiger tube and a Scaler model 181-A, Nuclear Chicago and radiocopper (copper sulfide) is gamma counted using a single pulse height analyser and a NaI(Tl) well type scintillation crystal.

## Experimental Part

### A. Samples and Standards Irradiation

Water samples (100 ml) are pipeted directly into polyethylene containers. The standards are prepared following the "internal standard method", by adding 1.00 ug. of chlorine as chloride and 1.00 ug. of copper to 100 ml. of the same water to be analysed, into a polyethylene container. Both polyethylene containers having the water sample and standard are irradiated during 35 minutes in a  $10^{13}$  n/cm<sup>2</sup>/sec. thermal neutron flux, using for this a special irradiation facility at the I.E.A.'s Swimming-pool Reactor, S.Paulo, Brazil.

### B. Chemical Treatment

After observing a cooling time of 10 minutes the sample is radiochemically treated. For this the sample is transferred into a 250 ml. beaker and 2 ml. of iron, chlorine, and copper carriers solutions are added. Then, the iron and copper hydroxides are precipitated by addition of 5 ml. of 10% NaOH solution. The beaker containing the precipitate is warmed at 80° C for a few minutes. The precipitate is filtered through a G-4 sintered glass crucible using vacuum and washed with water. The filtrate is kept for the copper analysis.

### Chlorine Separation

Three ml. of 70% HNO<sub>3</sub> and 2 ml. of silver nitrate carrier solution are added to the filtrate. The mixture is warmed

for a few minutes and the silver chloride is filtered off through Whatmann 42 filter paper. The precipitate is mounted for beta counting, after washed with alcohol and ether. The  $\text{Cl-38}$  activity is determined using an aluminum absorber of  $1310 \text{ mg./cm}^2$ .

### Copper Separation

The iron and copper hydroxides precipitate on the crucible is dissolved with 3 to 4 ml. of 12M HCl. The crucible walls are washed with water and the solution is transferred to a 50 ml. centrifuge tube. Iron is precipitated with  $\text{NH}_3$  gas, centrifuged, washed and discarded.

The supernatant containing the blue tetra-ammine copper complex is acidified with sufficient 12M HCl to have a final free acidity of 0.5 to 1.0 M HCl. Then the copper is precipitated as sulfide by bubbling  $\text{H}_2\text{S}$  gas. The copper sulfide is filtered on a sintered glass plate with Whatmann n<sup>o</sup> 42 paper, washed with water and alcohol. The filter paper containing the copper sulfide is transferred to a plastic vial and gamma counted at the 0.510 Mev peak (Cu-64, 12.8 hours half-life).

### C. Radiochemical Treatment for Standards

Standards of 1.00 ug. of Cl and Cu in 100 ml. of same water to be analysed are irradiated for the same time at the same geometry and neutron flux. The standards are processed in the same way as the samples.

### D. Chlorine and Copper Content

The amount of chlorine and copper in the samples are determined by the relation:

$$\frac{A_p}{A_a} = \frac{m_p + m_a}{m_a}, \quad \text{therefore:} \quad m_a = \frac{A_a}{A_p - A_a} \cdot m_p$$

where  $m_a$  = mass of Cl or Cu in the sample  
 $m_p$  = mass of Cl or Cu in the standard  
 $A_a$  = Cl or Cu activity in the sample  
 $A_p$  = Cl or Cu activity in the standard plus the Cl or Cu activity in the sample

## Results and Discussion

### 1. Chemical Yield

The recovery of Cl and Cu by the method here suggested was determined carefully; the chlorine yield was determined gravimetrically and the copper yield was determined using Cu-64 radioisotope as tracer.

#### Recovery of Chlorine

To various 100 ml. demineralized water aliquots 20.0 mg. of Cl (standard NaCl solution) were added, following the same chemical treatment as the irradiated samples. The final AgCl precipitate was washed with alcohol and ether, then dried in an air oven at 90° C and weighed. The chemical yield was determined by comparison with the amount of Cl added.

Table I shows the results correspondent to a series of chlorine determination:

TABLE I

Sample	Cl Added (mg.)	Cl Found (mg.)	Yield (%)
1	20.0	19.2	96
2	20.0	19.1	95
3	20.0	19.0	95
4	20.0	19.3	96
5	20.0	19.0	95

### Recovery of Copper

The yield of copper, as copper sulfide, was determined using Cu-64 (12.8 hours half-life) as tracer. To 100 ml. demineralized water samples 20.0 mg. of stable copper and 1.00 ug. of Cu-64 tracer were added, the radiocopper having an activity close to the induced copper activity in the sample. After adding the iron and chlorine carriers the iron and copper hydroxides were precipitated with a 10% NaOH solution. The resulted precipitates came through the same chemical treatment as described above for the separation of copper.

The final chemical yield for copper in the whole procedure was determined by comparison of the copper sulfides activities with the activity of 1.00 ug. of unprocessed copper (Table II).

As it can be seen in Table II the recovery of copper is high and reproducible.

TABLE II

Sample	Activity (cpm)	Cu Added (ug.)	Cu Found (ug.)	Chemical Yield %
1	4249	1.00	0.94	94
2	4246	1.00	0.94	94
3	4328	1.00	0.95	95
4	4213	1.00	0.93	93
Standard	4538	1.00	-	-

## 2. Reproductibility

Due to the relatively large volume of the polyethylene containers for the irradiation facility used it is necessary to irradiate the sample and the standard separately. This could introduce errors due to the flux fluctuation during the irradiation time and errors due to measurement of the irradiation time.

To verify the extension of the reproductibility of these results, as it was known dependable of factors cited above, various series of experiences were runned.

To various 100 ml. water samples with content of Cl and Cu negligible compared with the Cl and Cu added, 1.00 ug. of each element was added. The aliquots were irradiated along the operational period and submitted to the chemical treatment for the Cl and Cu separation described above. For each series of experiments the standard deviation was found to be about 5% for each one element. Tables III-1 and III-2 show the results of a typical series of experiments:

TABLE III-1

### Chlorine

Sample	Activity (cpm)	Mean Deviation (%)	Cl Found (ug.)
1	10806	0.2	1.00
2	11089	3.0	1.03
3	10827	0.4	1.00
4	10400	3.0	0.97
5	10760	0.2	1.00

Standard deviation =  $\pm$  0.02 ug.

TABLE III-2 - Copper

Sample	Activity (cpm)	Mean Deviation (%)	Cu Found (ug)
1	2200	3.7	1.04
2	2160	1.8	1.02
3	2050	3.4	0.97
4	2020	4.8	0.95
5	2180	2.7	1.03

Standard deviation =  $\pm$  0.04 ug

### 3. Sensitivity

The procedure here described allows to determine mass of Cl or Cu as low as 0.05 ug. The chemical procedure is very simple and fast, requiring only 25 minutes for a determination of chlorine and 40 minutes for copper.

### 4. Interferences

In the determination of Cl the possible interferences were eliminated with the aid of an aluminum absorber (1310 mg./cm<sup>2</sup>), sufficient to cut out beta particles of lower energy than 4.8 Mev (Cl-38). The half-life of Cl-38 was followed and found equal to 38 minutes, in good agreement with literature 37.3 minutes value.

In the determination of copper no interferences were found. The half-life of the copper precipitate was followed by gamma counting at the 0.510 Mev peak or by integrating the area under the peak. A value between 12.6 and 13.0 hours for the half-life of copper was found, therefore very close to the value 12.8

reported in the literature.

On the other hand Zn-65 (245 days) was used as tracer to verify a possible contamination in the copper precipitate, since zinc is an element that could be coprecipitated along with copper sulfide. Coincidentally Zn-65 has a gamma photopeak of 0.511 Mev. At the end of copper separation no Zn-65 contamination was found in the copper sulfide precipitate.

5. Results

Table IV contains the results of some Cl and Cu analysis carried out at the Instituto de Energia Atômica with the purpose to control the quality and purity of the Swimming-pool Reactor water.

TABLE IV

Date	Demineralized <sup>(5)</sup> Water (Primary System)		Swimming-pool Water		Secondary System (Recirculation) <sup>(5)</sup>	
	Copper (ppb)	Chlorine (ppb)	Copper (ppb)	Chlorine (ppb)	Copper (ppb)	Chlorine (ppb)
12/64	3.0	3.5	0.3	1.7	2.5	1.7
1/65	0.4	6.0	0.3	1.2	0.6	1.0
2/65	0.9	5.0	4.7	1.2	2.3	0.2
3/65	0.7	1.2	0.2	0.2	0.6	0.4
4/65	0.5	3.5	0.2	0.5	0.5	1.0

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