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Extraction and spectrophotometric determination of Hg^{2+} as complex anion HgI_3^-

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ABSTRACT: A method has been developed for the extraction and spectrophotometric determination of Hg^{2+} in a concentration range of 0.2-1.0 mg L^{-1} ; following the Lambert-Beer's law using high molecular weight quaternary ammonium salts dissolved in chloroform. The metal complex anion was determined in the extract in the region UV (260 nm).

KEYWORDS: Extraction; spectrophotometric determination; heavy metals; ion exchange.

Introduction

The problem of controlling microquantities of mercury in water ($> 10 \text{ mgL}^{-1}$), wastewater, surface waters, ground water etc.; due to the pouring of this metal by antropogenic activities (2, 3) has a special importance for the preservation of life. However, the achievement abstained in the determination of Hg^{2+} by combined atomic absorption spectrophotometric shows a necessity to develop another sensible and economic method that is more accessible to manufacturing laboratories and points of sanitary controls. Moreover the process of extraction can be used in the separation and concentration of this metal for the continuous monitoring of the environment. This paper describes a method for the extraction and spectrophotometric determination of Hg^{2+} as a complex triiodomercuriate (II) anion extracted from the organic phase with tetradecylammonium nitrate dissolved in chloroform.

Material an methods

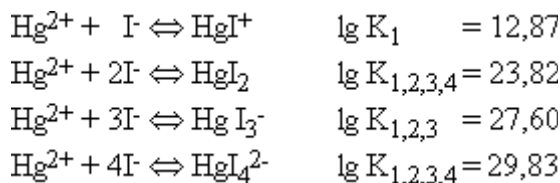
For the extraction and determination of Hg^{2+} the following reagents were used: HNO_3 , HgO ,

H₂SO₄, chloroform, all analytical grade, besides the tetradecylammonium nitrate 99% purity.

The spectrophotometric determinations were done using a CF-26 spectrophotometer in the UV-region at 260 nm with controlled temperature at 298 ± 1K. The standard solutions were prepared using Hg(NO₃)₂ at concentration of Hg²⁺ ions between 0.2-1.0 mg/L in the presence of iodide-ions 5.10⁻³ mol/L. The organic phase was prepared using tetradecylammonium nitrate as extractant dissolved in chloroform. The concentration of tetradecylammonium nitrate was 10⁻⁴ mol/L. In this concentration range Hg²⁺ follows the Lambert-Beer's law. For the extraction 10 ml of organic phase (tetradecylammonium nitrate dissolved in chloroform.) in 100 ml of sample was used and this was prepared under the conditions described before.

Results and Discussion

The capacity of Hg²⁺ to form stable complexes with halides and specifically with I⁻ is well known. In the presence of the iodide anion the formation of complexes at the following phases occurs.



Where the total concentration of Hg²⁺, C(Hg²⁺)_T is equal to:

$$C(\text{Hg})_T = C(\text{Hg}^{2+}) + C(\text{HgI}^+) + C(\text{HgI}_3^-) + C(\text{HgI}_4^{2-}) \quad (1)$$

Where the forms Hg²⁺, HgI⁺, HgI₂, HgI₃⁻, HgI₄²⁻ prevailing one or other depends on the concentration of the ligand. If the concentration of iodide ion is more than 10⁻³ molL⁻¹ then the following occurs.

$$C(\text{Hg})_T \gg C(\text{HgI}_3^-) + C(\text{HgI}_4^{2-})$$

the forms HgI₃⁻ and HgI₄²⁻ may be extracted by an anionic exchange mechanism.

The distribution function F(HgI₃⁻) was determined when the upper iodide concentration (5.10⁻³ mol.L⁻¹) prevailing under this condition (more than 75% of HgI₃⁻ complex) was obtained.

$$\begin{aligned} &K_{1,2,3} e^{3(I)} \\ \Phi_{\text{HgI}_3^-} &= \frac{K_{1,2,3} e^{3(I)}}{1 + \sum_{i=1}^4 k_{1-i} C^i(I)} > 75\% , i = 1 \dots 4 \end{aligned} \quad (2)$$

High concentration > 5.10⁻³ mol L⁻¹ of iodide present the following inconvenient that affects the

results from an analytical point of view;

fundamental reaction



where Q^+ = tetradecylammonium cation

collateral reaction



If the concentration of iodide ion is relatively high increase $> 5 \cdot 10^{-3} \text{ mol L}^{-1}$ there will be an increase in the collateral reaction (4) thus affecting the absorbance value already this compound absorbs in 260 nm. The formation of the complex anion HgI_4^{2-} may occur with the subsequent variation of the fundamental reaction (3). This collateral effect when the concentration of iodide ion is $5 \cdot 10^{-3} \text{ mol L}^{-1}$ is eliminated, by adding nitrate ion with a concentration of 0.4 mol L^{-1} , without affecting the equilibrium of the fundamental reactions (3) due to the extraordinary high affinity of the HI_3^- complex for the tetradecylammonium (Q^+) cation because of the superior hydrophobicity of the HgI_3^- in comparison with the NO_3^- .(5)

In this way, using a ligand concentration equal to $5 \cdot 10^{-3} \text{ mol L}^{-1}$ and concentration of nitrate anion 0.4 mol L^{-1} and introducing in this solutions, samples of Hg^{2+} at $\text{pH} = 5$ the optimum conditions are reached for the extraction process, i.e. $C(\text{Q}^+\text{NO}_3^-) = 10^{-4} \text{ mol L}^{-1}$ in the organic phase. If the concentration of Hg^{2+} are with in the range of $0.2\text{-}1.0 \text{ mg L}^{-1}$, the linear equation obtained in this case is.

$$y = 0.0162 + 16685 x \text{ (Figure 1)}$$

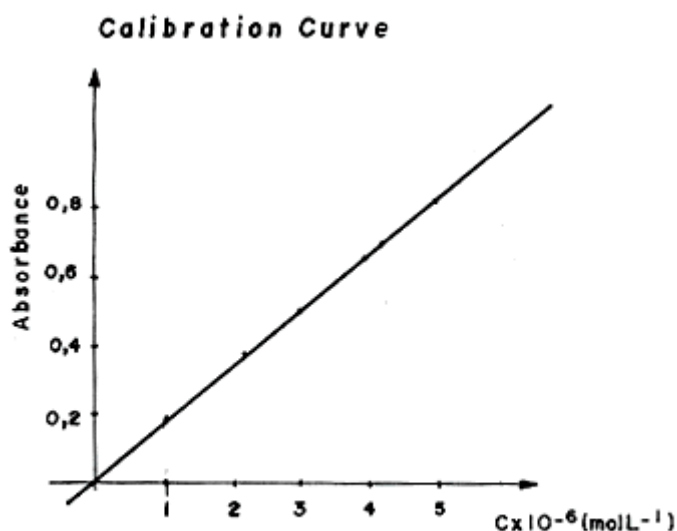


FIGURE 1 - Calibration curve.

with a correlation coefficient equal to 90.9928. The grade of interference was determined with some

metals, ie Zn^{2+} , Cu^{2+} , Fe^{2+} , Ag^+ doesn't interfere when their concentration is equal or superior to the concentration of Hg^{2+} in the sample below 1.0 mg L^{-1} . The absence of interference is due to the high stability of the mercury complex with the iodide in comparison with these metals. The organic material present in the sample interferes strongly. It is necessary before extraction to treat the solution, to be analyzed with 10 ml of chloroform several times until the total absence of organic material at 260 nm is obtained.

Conclusions

A selective and quick method is developed for the determination of Hg^{2+} a triiodomercuriate complex anion by employing as extractant a quaternary alkyl ammonium salt dissolved in chloroform.

This method permits determining the concentration of Hg^{2+} below 0.2 mg L^{-1} which makes this methods very effective and with minimum interference by heavy metals. Preconcentration of the sample is necessary when the concentration of Hg^{2+} is less than 0.2 mg L^{-1} in accordance with Lambert-Beer's law.

FERNÁNDEZ TERRA, Z., DEL TÓRO DÉNIS, R., VARELA DE MOYA, H. Extração e determinação espectrofotométrica de Hg^{2+} como o ânion HgI_3^- . *Ecl. Quím. (São Paulo)*. v.22, p.9-14, 1997.

RESUMO: Foi desenvolvido um método para a extração e determinação espectrofotométrica de Hg^{2+} em um intervalo de concentração de $0,2-1,0 \text{ mg L}^{-1}$, seguindo a lei de Lambert-Beer, usando sais de amônia quaternários de peso molecular elevado. A determinação do ânion metálico complexo, no extrato, foi feita na região do UV (260nm).

PALAVRAS-CHAVE: Extração; determinação espectrofotométrica; metais pesados; troca iônica

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