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Potentiometric titration of methylmercury solutions - a standardization procedure

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ABSTRACT. Methylmercury solutions in chloroform (1000 mgHg/L) were titrated potentiometrically, using saturated calomel and silver electrodes, and potassium iodide aqueous solution (5 mmols/L) as the titrant. For comparison, mercuric ion and methylmercury aqueous solutions were also titrated, under the same conditions. The proposed procedure showed that the standardization of organomercurial solutions is possible, with great exactness, avoiding any oxidative pre-treatment.

Key words: standardization, methylmercury solutions, potentiometric titration.

RESUMO. Titulação potenciométrica de soluções de metilmercúrio – um procedimento para padronização. Foram realizadas titulações potenciométricas de soluções de metilmercúrio em clorofórmio (1000 mgHg/L), usando eletrodos de prata e de calomelano, e tendo soluções aquosas de iodeto de potássio como titulante (5 mmoles/L). Nas mesmas condições, soluções aquosas do íon mercúrico e de metilmercúrio foram, também, tituladas. O procedimento proposto mostra ser possível a padronização de soluções de organomercuriais, com grande exatidão, sem a necessidade de etapas preliminares de oxidação.

Palavras-chave: padronização, soluções de metilmercúrio, titulação potenciométrica.

Mercury is unique in many of its physicochemical properties and occupies a singularly important place in the present state of human technological existence. Not surprisingly, the literature on the environmental and physiological occurrence of mercury is extensive.

Methylmercury is one of the most toxic forms of mercury, causing irreversible damage to the central nervous system. The discovery in the 1960's of methylmercury in fish taken from waters having no known source of this organomercurial caused widespread concern about a general threat to public health (Eisler, 1987). Subsequent research revealing both enzymatic and non-enzymatic pathways to which microorganisms can methylate inorganic and metallic mercury provided a stimulus for research on the chemistry and biochemistry of methylmercury (Rabenstein, 1978).

The first basic procedure for determining mehtylmercury was developed by Westöo (1968); since then, several specific variations of this procedure have appeared for methylmercury analysis in fish, sediment, urine, hair and blood. Generally an initial extraction of methylmercury as a halide with organic solvent is employed, followed by gas chromatography, mass spectrometry or cold vapor atomic absorption spectrometry analysis. The organomercurial can be determined in an organic solution, or in the re-extracted aqueous layer.

As a rule, stock solutions are prepared from methylmercury halides (or hydroxide converted to halide by acid addition), by dissolving the salt in water, sodium carbonate solution or an organic solvent, as benzene or chloroform. Working standards are prepared from the stock solution by appropriate serial dilution.

Organomercury solutions standardization procedures are not known, mainly in non-aqueous solvents. Velghe and co-workers (1978) used potentiometric titrations to determine the purity of mercury compounds, and this procedure involved an oxidation step with permanganate solution. However, any oxidative treatment is tedious, time consuming and critical, due to loss or contamination possibilities.

Once in many analytical procedures methylmercury compounds are determined in an organic medium and being its solutions in chloroform stable for, at least, two months (Resende, 1992), the potentiometric titration of the

organomercurial, directly, without any oxidation step, was evaluated. A relevant characteristic of methylmercury is its great tendency to form complexes with coordination number equal to one, as in the hydroxide, nitrate and halides species (Rabenstein, 1978). Considering the stability constants for the different methylmercury halides (Sillén and Martell, 1971), a potassium iodide aqueous solution was chosen as titrant. The titration end point corresponds to the formation of methylmercury iodide, according to the equation:

$$CH_3Hg^+_{(sol)} + I^-_{(sol)} \Leftrightarrow CH_3HgI_{(sol)}$$

Materials and methods

Reagents. Methylmercury stock solutions were prepared dissolving the chloride salt (Flücka, 98%) in distilled deionized water or in chloroform; these solutions were kept in dark glass flasks and stored at 4ºC. Mercury (II) solution was prepared dissolving the nitrate salt (Merck, 99%) in distilled deionized water.

Aqueous potassium iodide and sodium chloride solutions were standardized by potentiometric titration with silver nitrate.

Chloroform and dimethylformamide, DMF, were of A.R. purity, and used without purification.

Apparatus. The potentiometric titrations were carried out with a pHmeter Alphalab PA 200 equipped with a calomel electrode and a silver electrode as reference and indicator electrodes respectively.

Procedure. Mercury (II) titrations were carried out at pH 3.5, with sodium chloride solution and using diphenylcarbazide as visual indicator (Meites,1963); for comparison, the same solution was titrated with potassium iodide solution, but using potentiometric measurements.

Methylmercury potentiometric titrations were carried out in water and in chloroform solutions, with aqueous potassium iodide as titrant. In the organic medium, the titrations were repeated in the presence of DMF.

Methylmercury aqueous and organic solutions were also submitted to an oxidative pre-treatment with a mixture (1:1) of nitric and sulphuric acids. The resulting mercury (II) ion was, then, determined by means of the potentiometric titrations with potassium iodide.

Each titration, for each particular system, was repeated at least three times.

Results and discussion

Typical titration curves for inorganic and organic mercury are presented in Figures 1-3. For each experiment the end point volume was located from the second derivative curve.

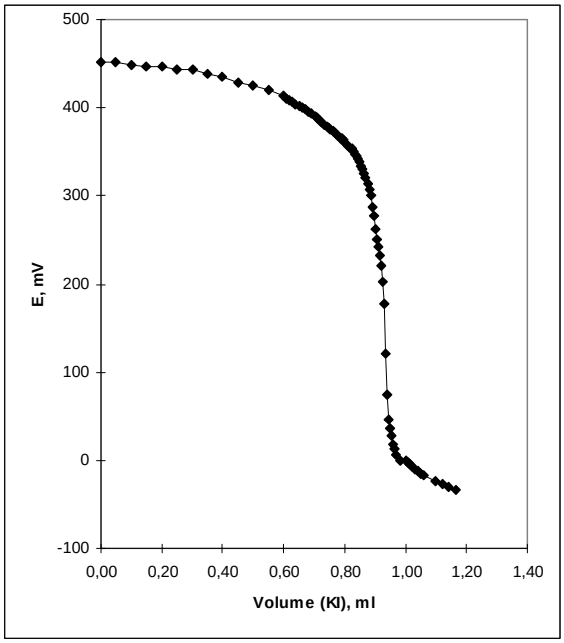

Figure 1. Titration curve for mercuric ion with potassium iodide

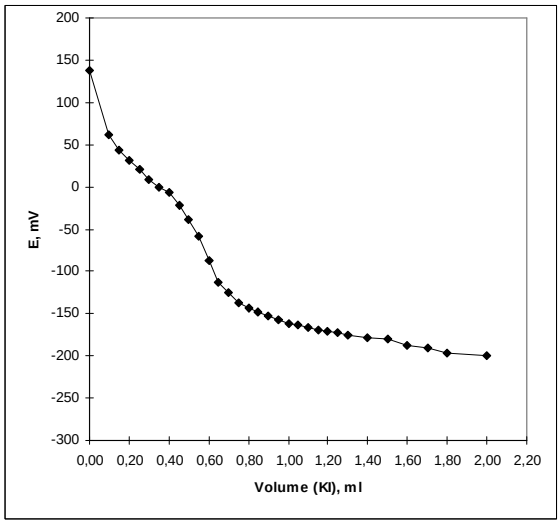

Figure 2. Titration curve for aqueous methylmercury solution with potassium iodide

Mercury (II) concentration in the aqueous solution, determined by visual or by potentiometric titrations, was identical, as pointed out in Table 1, and this agreement shows the exactness of the potentiometric determination.

When titrating aqueous methylmercury solutions the results obtained for mercury concentration, showed in Table 2, were the same with or without the oxidative pre-treatment, and the statistical T-test (Skoog and West, 1982) confirmed the good equivalence for the average concentrations determined.

Table 1. Mercuric ion titration (5.85 mmols Hg^{2+}/L)

	mmols Hg^{2+}/L (*)
visual titration with NaCl (n=3)	5.83±0.03
potentiometric titration with KI (n=5)	5.82±0.12

n: number of determinations; (*): average concentration ± standard deviation

Table 2. Methylmercury Titrations by Potentiometry with KI

	mmols Hg/L (*)
aqueous solution (6.17 mmols Hg/L)	
without digestion step (n=4)	6.09±0.15
with digestion step (n=3)	6.10±0.11
organic solution (3.64 mmols Hg/L)	
without digestion step (n=7)	3.76±0.18
with digestion step (n=3)	3.60±0.06

n: number of determinations; (*): average concentration ± standard deviation

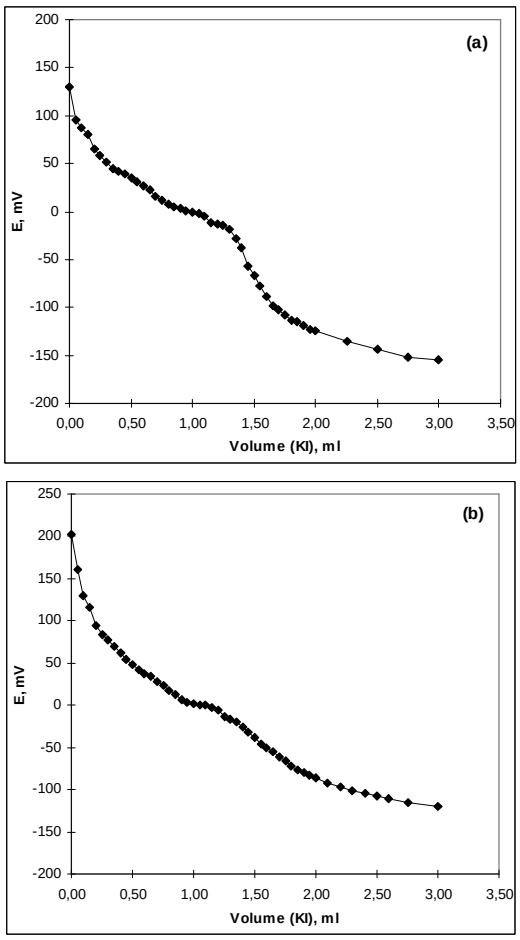

Figure 3. Titration curves for organic methylmercury solution with potassium iodide. (a) with H_2O addition; (b) with H_2O + DMF addition

As still indicated in Table 2, mercury concentration can be determined with great exactness, directly, without any pre-treatment, also in the organic solution, using the same simple potentiometric procedure with aqueous iodide solution. So, it can be concluded that the oxidative step is not necessary at all for accurate determinations of methylmercury forms, in either aqueous or organic solutions. The agreement verified in the mercury concentrations values obtained after a digestion step and without this treatment indicates the accuracy of the procedure.

It is known that DMF can be used to improve the miscibility of two different solvents, as water and chloroform. Thus, methylmercury titrations in chloroform were conducted with the addition of water and also in the presence of a water-DMF mixture (1:1). Comparing the results obtained from these titrations conditions, presented in Table 3, it can be seen that the average values are identical, being the differences related to randomic errors. Consequently, the potentiometric titration of methylmercury organic solutions can be feasible with just water addition.

Table 3. Methylmercury titration (3.64 mmols Hg/L): DMF effect

	mmols Hg/L (*)
addition of H_2O (n=4)	3.71±0.15
addition of H_2O and DMF(n=3)	3.82±0.20

n: number of determinations; (*): average concentration ± standard deviation

The methylmercury titration as proposed seems to be suitable as standardization procedure, as it exhibits accuracy and precision, and avoids the problems resulting from contamination or poor recuperation that can occur in oxidative step-involving procedures.

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