

MERCURY DETERMINATION FROM INCIDENTALLY POLLUTED WATERS BY COLLECTING GRAVIMETRY IN ORGANIC STAGE METHOD

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ABSTRACT

Determination of mercury in incidentally polluted waters, presented in CALIST Program, was carried out using tiobis-β-naphthol as a reagent. The method proposed for mercury determination, named “collecting gravimetry in organic stage” is original, thus being superior to other simpler methods used in laboratory.

KEYWORD: Mercury, tiobis-β-naphthol, quantitative analysis, incidentally polluted waters

1. General considerations

Polluting by heavy metals is considered to be a major issue. Mercury concentration increasing in water is a consequence of both industrial pollution (specially by mineral derives) and agricultural one (organic-mercurial derives). In water, these derives decompose in organic products which progressively change in methyl-mercury, the simplest but the most toxic derive.

The methods for determination of mercury from waters, found in the technical literature, including those standardized, are laboriously, and require a large quantity of work intended for achieving of each stage. At the same time, they use different reagents as well as separation and shielding methods as a result of negative foreign water ions interference and sufficient non-specificity of reagents.

Researches carried out by CALIST program propose an original method intended for determination of mercury from incidentally polluted waters.

Therefore, tiobis-β-naphthol (proposed reagent) forms by Hg (II) insoluble compounds, both in water and in mostly usually solvents tested.

As a result of researches carried out it was settled that the reagent, dissolved in n-propyl carbinol, extracts these ions from solution as steady in time precipitates and constant chemical composition.

Method called “collecting gravimetry in organic stage” focuses a lot of qualities:

- The got precipitates are distinctly pure; so, tiobis-β-naphthol being soluble in n-propyl carbinol and the possibility of polluting the precipitate by reagent is excluded.
- Operation methodology suggested in this paper decreases very much each of gravimetry determination stages. In this way, determination methods proposed for copper (II), mercury (II) and lead (II) join the accuracy and simplicity of gravimetrical methods with analyses performing rapidity by other procedures;
- Metal exhaust from watery medium and adjusting the suitable pH increase the selectivity;
- Increasing the local precipitate quantity the reaction sensitivity enlarges very much. As a result of extraction, the metallic ion from diluted solution is lumped in a small solvent volume, therefore, getting the conditions of reaching the solubility product and so the precipitation.
- solubility of precipitates formed in n-propyl carbinol is smaller than in partly watery solvents; the smaller dielectric constant decreases the dissociation degree and therefore the solubility.

2. Determination of mercury in waters

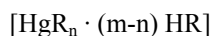
The suggested method intended for mercury determination is selective; in running conditions given in the paper, Hg(II) only precipitates. Therefore, it proves to be better than other usual methods applied in laboratory.

2.1. Required conditions for operation mode set up

➤ Compound raw formula set up

As compound between tiobis-β-naphthol and Hg (II) was discovered by the professional university staff, several additional researches were required to set up its structure and formula in order to be used in chemical analysis. Aiming this goal the researches given below were performed.

a) Hg (II) ion forms together with tiobis-β-naphthol a yellow colored compound in acid medium, a few soluble in water and in usually solvents. When tiobis-β-naphthol dissolves in n-propyl carbinol this one has the capacity of exhausting the Hg (II) ions from watery solutions and forms a light yellow precipitate in organic solvents. It is supposed that a neutral compound by general composition forms:



with extraction equilibrium described by equation:



where:

HR corresponds to the reagent with the raw formula :

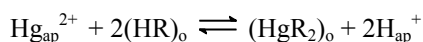


ap index – watery phase;

o index – organic phase.

In order to set up the Hg (II) exhaust by tiobis-β-naphthol using n-propyl carbinol as water non-miscible solvent, the experimental and calculation model was used in case of extraction system by chelate compounds.

Therefore, it was set up that Hg (II) extraction by tiobis-β-naphthol at pH = 1 – 2 is made based on the following equilibrium.



b) The precipitate formed in organic phase was separated, washed by acetone and dried in air. Chemical analysis emphasized a new compound forming with raw formula: Hg (C₂₀H₁₃O₂S)₂. Its results are shown in table 1.

Table 1

| Chemical analysis | C [%] | H [%] | S [%] |
|----------------------|-------|-------|-------|
| Calculated | 57.31 | 3.14 | 7.68 |
| Experimentally found | 58 | 3.20 | 8.01 |

➤ Influence of pH

Following the variation of repartition coefficient and exhaust percentage implicitly, depending on pH value, it may be noticed that for ratio $C_{\text{HR}}/C_{\text{Hg}^{2+}} = 10/1$ (where: C_{HR} – reagent concentration in organic phase and $C_{\text{Hg}^{2+}}$ - Hg²⁺ ion concentration in watery phase), the extraction percentage increases by pH. A larger exhaust percentage than 99% is obtained beginning with pH = 1.7 (fig.1).

Practically quantitative extraction, as a steady composition precipitate of Hg²⁺ ion existing in watery solution, suggested the idea of using this operation system in order to set up a separation method of Hg²⁺ ion from these watery solutions and gravimetric processing of the extract obtained.

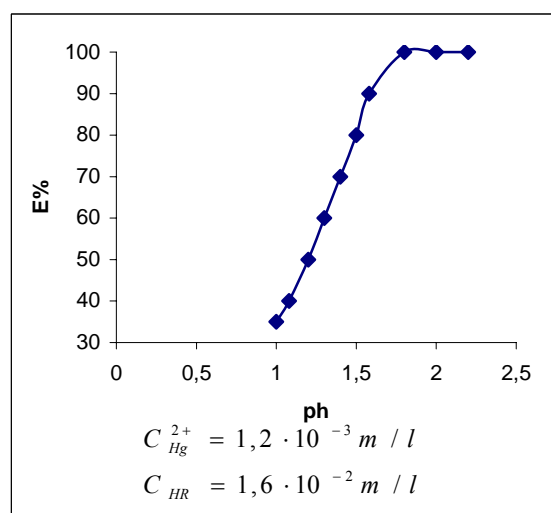


Fig. 1. Variation of the exhaust percentage by the watery phase pH.

➤ Temperature influence

In order to characterize the compound obtained with mercury, intended for use in quantitative analysis by the proposed method (collecting gravimetry in organic stage), the heating behavior was studied by derivative-graphical analysis.

Thermal-gravimetric study made in dynamic temperature conditions by steady heating speed allowed to get some information about thermal stability of the investigated combination, chemical composition and thermal decomposing kinetics.

At the same time, as a result of experiments, it was set up that at 102°C the compound (mercury tiobis-β-naphthol) begins to decompose; so, drying in the oven will be made up to 90°C, that is enough temperature to eliminate the acetone used as flushing agent.

2.2 Checking the proposed method – experimental

Operation mode. The following will be supplied in a 250 ml separation hopper: 100 ml solution to be analyzed brought to $\text{pH} = 1 \div 2$ which contain a known quantity of mercury ions ($2.4 \div 3.4 \text{ mg Hg}^{2+}$), 10 ml solution of reagent in n-propyl carbinol, $1.6 \cdot 10^{-2} \text{ mole/l}$ (5.088 g tiobis- β -naphthol / l), 5 ml solution of potassium nitrate 1 n, 2 ml buffer solution, then 5 minutes stirring. After phases separation, the precipitate got in organic solvent is filtered on vacuum spout by G_4 filtering crucible.

Precipitate traces which remain sticky on the hopper walls will be entirely passed in crucible helped by 2-3 stirrings and washing by acetone. The crucible with precipitate dries in oven for approx. 10 minutes at $80 \div 90 \text{ }^\circ\text{C}$ temperature, cools down in special vessel and is weighed.

Experimental determinations proved that compound formation and extraction are performed in high speed, therefore, in order to settle down the equilibrium, a few minutes are sufficiently.

Total precipitation checking is traced by repeating the extraction operation from watery solution, separated from the first solution.

Using for extraction 10 ml solution of tiobis- β -naphthol in n-propyl carbinol, $1.6 \cdot 10^{-2} \text{ mole/l}$ respectively, good results got for a precipitate weighed in $0.0100 \div 0.0160 \text{ g}$ range.

Experimental determination are alike the provisions made, the lower limit being conditioned by analytical balance accuracy where the weighting were performed, and the upper limit of maximum reagent solubility in n-propyl carbinol, being that one required for providing the ratio $C_{\text{HR}}/C_{\text{Hg}^{2+}} = 10/1$ (where: C_{HR} – reagent concentration in organic phase and $C_{\text{Hg}^{2+}}$ – Hg^{2+} ion concentration in watery phase), favorable for extraction and precipitation.

In order to calculate the accuracy of gravimetric method the procedure of comparison of pair samples was used. This procedure may be used also for adjusting a new method, making determinations in a wide range of concentrations and comparing the pair values, "the found" value against "the taken" one – exactly known.

In conclusion, the precipitate with formula HgR_2 got by this method is pure, has a steady composition and may be processed by quick gravimetric determination. The gravimetric factor ($f = M_{\text{Hg}}/M_{\text{HgR}_2}$; $f = 0.2401$ respectively) is convenient for this kind of determinations. The method offers very good selectivity and small execution time.

Filtering and washing of precipitate, separated in a small volume of organic solvent is quickly, and thus allows the performance, in a short time of large watery solution volumes having small mercury content (II). For example, at 10/1 phases ratio,

mercury (II) may be separated and determined, with good results, from 0.02 mg/l concentration solutions.

2.3 The method application - mercury determination from incidentally polluted waters

Usually, mercury from natural waters is either lacking or may be found in small concentration ($< 0,1 \mu\text{g/dm}^3$). The danger of increasing the mercury concentration in water is due to both industrial and agricultural pollution. The permitted mercury limit allowed in industrial and domestic waste water exhausted in natural receivers, according NTPA–001/2002, is 0.05 mg/l . Because of this, it was required to determine the mercury even in small quantities, in water, in order to prevent some incidentally contamination.

In case in which the mercury quantity from analyzed sample is beneath 0.02 mg/l the *additions method* will be used, which is often used in chemical analysis practice of element traces.

Operation mode. In order to apply the method proposed in hereby stage, a reaction is made previously for mercury ion identification in water.

In a 500 ml separation hopper a necessary and sufficiently water analyzing volume is feed (depending on the probably mercury content in water) which is noted as V_1 . Solution is brought to $\text{pH} = 1 \div 2$ and $10 \div 50 \text{ ml}$ solution of reagent in n-propyl carbinol, $1.6 \cdot 10^{-2} \text{ mole/l}$ (5.088 g tiobis- β -naphthol / l), 5 ml solution of potassium nitrate 1 n and 2 ml buffer solution are added and stirred for $5 \div 10$ minutes.

After the phases separation, the precipitate got in organic solvent is filtered in vacuum spout by G_4 filtering crucible. The precipitate traces which remain sticky on the hopper walls will be entirely passed in crucible, helped by 2-3 stirrings and washing by acetone. The crucible with precipitate dries in oven for approx. 10 minutes at $80 \div 90 \text{ }^\circ\text{C}$ temperature, cools down in special vessel and is weighed.

• *Calculation of mercury quantity from analyzed sample*

$$X_{\text{Hg}} = 1000 \cdot p \cdot f / V_1 \text{ [g/l]}$$

where: f – gravimetric factor, $p = 0.2401$;
 p – precipitate quantity got, g;
 V_1 – water volume taken in sample

The method was checked on two samples where known quantities of Hg (II) together with ions of Ag(I), Pb(II), Fe(II), Ca(II), Ba(II), Mn(II), Mg(II) and Cu(II) were added and which form chemical compounds with tiobis- β -naphthol but not at pH used for determination of Hg(II).

The compound formed by Fe (III), at $\text{pH} = 2$, is extracted in n-propyl carbinol but is soluble; for the excessive reagent used, it does not prevent the

mercury (II) determination up to the ratio Fe(III)/Hg(II) = 10/1 studied.

Statistically processing of experimental results (table 2) got on samples with known composition shows that the proposed method is accurate ($t_{\text{exp}} < t_{95\%,9}$) and is not affected by systematic errors (table 3 for specimen 1 and table 4 for specimen 2).

The real mercury content, in samples that simulate a polluted water, frames in the experimentally determined trusty range limits.

Table 2

| Sample code | Average content (mg Hg/ sample) | |
|----------------|---------------------------------|------------|
| | Specimen 1 | Specimen 2 |
| n ₁ | 2.90 | 3.86 |
| n ₂ | 2.92 | 3.78 |
| n ₃ | 2.89 | 3.80 |
| n ₄ | 2.86 | 3.94 |
| n ₅ | 2.82 | 3.82 |
| n ₆ | 2.85 | 3.88 |
| n ₇ | 2.94 | 4 |
| n ₈ | 3.02 | 3.72 |

Table 3

| Statistical parameters | Parameter | Analyzed sample |
|---|-----------------------------|--------------------------------|
| | | Specimen 1 |
| Real content (mg Hg/sample) | A | 2.95 |
| Number of determinations | N | 8 |
| Average content (mg Hg/ sample) | \bar{x} | 2.9 |
| Dispersion of selection | S ² | 0.0038 |
| Standard deviation | S | 0.616 |
| Quadratic average error of mean selection | S _x ⁻ | 0.02177 |
| t _{exp} | t _{exp} | 2.29 |
| t _{p%} k = (n-1) | t _{95,7} | 2.37 |
| Individual values spreading | $\bar{x} \pm \Delta X$ | 2.9 ± 0.141 (3.041 – 2.759) |

Table 4

| Statistical parameters | Parameter | Analyzed sample |
|---------------------------------|----------------|-----------------|
| | | Specimen 2 |
| Real content (mg Hg/sample) | A | 3.83 |
| Number of determinations | N | 8 |
| Average content (mg Hg/ sample) | \bar{x} | 3.85 |
| Dispersion of selection | S ² | 0.008 |

| | | |
|---|-----------------------------|---------------------------------|
| Standard deviation | S | 0.09 |
| Quadratic average error of selection mean | S _x ⁻ | 0.0318 |
| t _{exp} | t _{exp} | 0.629 |
| t _{p%} k = (n-1) | t _{95,7} | 2.37 |
| Individual values spreading | $\bar{x} \pm \Delta X$ | 3.83 ± 0.056 (3.886 - 2.774) |

where:

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}; \quad S^2 = \frac{\sum_{i=1}^n (\bar{x} - x_i)^2}{n-1}$$

$$S = \sqrt{S^2}; \quad S_x^- = \frac{S}{\sqrt{n}}$$

$$t_{\text{exp}} = \frac{|A - \bar{x}|}{S_x^-}; \quad \Delta x = \pm t \cdot S$$

$$\Delta \bar{x} = \pm t \cdot S_x^-$$

2.4 Conclusions

- A solution of tiobis-β-naphthol in n – propil carbinol extracts Hg (II) from watery solution; in organic phase, a pure steady precipitate forms with well defined composition .

- The obtained compound may be processed by „collecting gravimetry in organic stage”. Filtering and washing the precipitate, in a small volume of organic solvent, are quickly and allow, in a short time, lumping of mercury from large volumes of watery solutions.

- Extraction and variation of pH allowed to increase the sensitivity and selectivity of determination.

- The method was applied for quickly analyzing of Hg (II) from incidentally polluted waters.

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