

Complexometric Determination of Mercury Based on a Selective Masking Reaction

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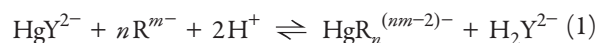
In undergraduate analytical chemistry courses, students usually perform well-defined laboratory activities using synthetic solutions and sample mixtures prepared by the instructors. The laboratory activities are rarely based on real samples. From this diagnostic, we implemented an optional activity at the end of the first analytical chemistry course. We suggested that the students propose a lab project that awakens their curiosity and perform it with the instructor's supervision. The project described here was one of the most interesting proposed experiments.

In the introduction to complexometry, the reaction of ethylenediaminetetraacetic acid (EDTA) with numerous common polyvalent cations and its use in titrations are discussed. Back titration and masking agents to improve the determination selectivity of specific metals is described in analytical textbooks (1–3). In this *Journal*, Ueno described the appropriate pH's and metal indicators for EDTA titrations (4) and Ramsay proposed a theoretical and practical study of the EDTA titration of cadmium and mercury (5).

In this project, students proposed a procedure for the complexometric determination of mercury in mixtures containing other polyvalent cations to investigate the potential environmental leaching of mercury from common 12 V batteries that were improperly disposed. To simulate this situation, batteries were submerged in water for one month. The project consisted of an initial experimental design; a bibliographic search about classical methods for mercury ion detection; choice and optimization of the selected technique with standard solutions, pretreatment and analysis of "real" samples, and conclusions.

Student Project Overview

Direct complexometric determinations of mercury are not possible owing to the lack of a specific metal indicator of the end point and to poor selectivity (6). Usually, an excess of EDTA is added to a mixture containing mercury, and the unreacted excess of EDTA is back titrated with a standard solution to determine the total amount of complexed cations. Then, some selective masking reagent R^{m-} is added to displace the mercury from the EDTA complex and the released EDTA is titrated with a standard solution, according to the following equilibria, where Y is EDTA:



Several displacement reagents of the mercury in the EDTA complex have been proposed in the literature (7, 8 and references cited therein). They include compounds containing sulfur (such as thiosemicarbazide, cysteine, thiourea, 2-mercaptoethanol, etc.), acetylacetone, dithizone, and inorganic anions.

However, interferences of metals such as Cu(II), Ag(I), Tl(III), and Pd(II) are possible with the use of some masking reagents. Other reagents are based on decomposition reactions of the chelate and precipitation of HgS in tedious and time consuming techniques.

As part of this project, students had to critically select one displacement reagent. They based their choice on the comparison between the conditional equilibrium constants of the Hg–EDTA complex at a slightly acidic pH (pH = 5.50) and those corresponding to the $\text{HgR}_n^{(nm-2)-}$ complexes. Larger differences between the constants lead to more quantitative displacement of eq 1 towards products. The complex formation constants of Hg(II) with some of the proposed displacement reagents are gathered in Table 1. Based on these equilibrium constant values, the possible masking agents that form significantly more stable complexes than the Hg–EDTA chelate are bromide, cyanide, iodide, thiosulfate, thiocyanate, and thiourea.

The potential interferences from other metallic ions, which would be also displaced from the EDTA chelates by the displacement reagents, were also taken into account. For the analysis of possible interferences, the students critically compared the stability constant of several chelates of cations with EDTA to those of the ions and some masking reagents. The comparison is graphically presented in Figure 1. It can be seen that cyanide forms highly stable complexes with Hg(II), which can displace the mercury in the EDTA complex, but the same applies to other cations, that is, the protocol using cyanide lacks selectivity. Thiourea as displacer would be interfered by Cu(II), if present. Cu(II), Co(II), Ni(II), and Fe(III) interferences would be

Table 1. Complex Formation Constants and Conditional Constants of Hg(II)

Ligand	Log	K_2	K_3	K_4
EDTA (pH 5.5, $\alpha_4 = 1.47 \times 10^{-6}$)	21.7			
Nitrite	NA	NA	NA	13.5
Thiosulfate	NA	29.2	30.6	
Sodium sulfide	NA	12.5		
Thiocyanate	NA	17.2	20	21.8
Bromide	9.4	18	20.7	22.2
Cyanide (pH 5.5, $\alpha_1 = 1.26 \times 10^{-4}$)	17	32.8	36.3	39
Thiourea	NA	21.3	24.2	25.8
Acetylacetone	21.7			
Iodide	12.9	23.8	27.6	29.8

NOTE: Data taken from refs 1, 9, and 10. NA indicates that the data was not available.

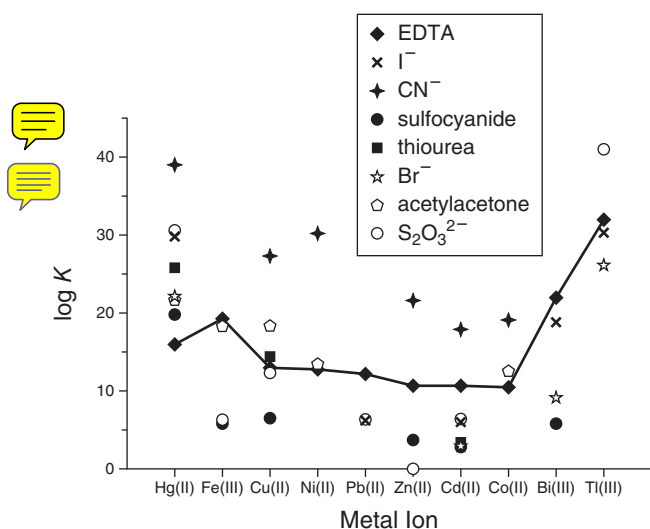


Figure 1. Comparison of stability constants of metal ions with different ligands.

expected with the use of acetylacetonate. Thallium (III) ion, if present, interferes with thiosulfate as displacement agent.

Based only on these thermodynamic considerations, bromide and iodide anions could be selected. Since iodide anions form more stable Hg-complexes than bromide anions, the former is preferred. No other practical considerations, such as reaction kinetics, were taken into account with the displacement reagent choice. After the analysis of the possible equilibria involved, the students design a protocol using potassium iodide as displacement reagent.

Experiment

Standard Solutions

An excess of about 0.25 mmoles of EDTA solution (10.00 mL of a 0.040 M standard solution) is added to an aliquot of an acidic solution containing Hg(II) ions and diluted to about 100 mL. The pH of the solution is adjusted to 5.50 using 0.5 M acetic acid/sodium acetate buffer solution, and about 0.02–0.03 mg of xylanol orange indicator is added. The excess of EDTA is titrated using standard zinc sulfate solution (0.026 M) until the end point is reached. An excess of solid potassium iodide is added to this solution and the flask is gently mixed by shaking. The solution turns immediately a distinguishable yellow. The released EDTA is titrated with the standard zinc solution to a sharp orange end point.

Battery Samples

Three battery samples were examined: four 12 V batteries were submerged in 1 L of distilled water; four batteries were submerged in 1 L of acidic distilled water at pH 5 in plastic bottles; and four batteries were crushed and submerged in 1 L of distilled water. The submerged battery samples were kept at room temperature for 30 days. The residual water containing the submerged batteries was carefully filtered and a 100 mL aliquot was analyzed by following the protocol for the standard solutions.

Complete experimental procedures, reagents, and sample preparations, along with the waste disposal indications are de-

Table 2. Results of Determination of a Hg(II) in a Synthetic Solution

Trial	$V_{\text{EDTA}}/\text{mL}$	$V_{\text{ZnSO}_4}/$ (first)	Total Ions/ mmol	$V_{\text{ZnSO}_4}/$ (second)	Hg(II)/ mmol
1	10.00	9.72	0.147	5.65	0.147
2	10.00	9.70	0.148	5.64	0.147
3	10.00	9.75	0.146	5.65	0.147
4	10.00	9.71	0.148	5.73	0.149
5	10.00	9.65	0.149	5.75	0.149

tailed in the online material

Hazards

Mercury is a volatile pollutant that can cause serious effects on the environment and human health. Excellent reference surveys on mercury as a contaminant can be found in (11, 12). Extreme care must be taken when these solutions are handled and disposed of. Disodium dihydrogen ethylenediaminetetraacetate dehydrate, zinc sulfate heptahydrate, sodium acetate trihydrate may cause eye, skin, and respiratory tract irritation. Hydrochloric acid is corrosive and damaging to skin, eyes, and lung irritant. Solid potassium iodide is a possible skin and lung irritant. Xylanol orange poses slight risk to students. Protective gloves and goggles must be always worn in the laboratory. Waste solutions were disposed of in special containers used for heavy metals.

Results

Standard Solutions

The determination of Hg(II) content in standard synthetic solutions is shown in Table 2. Since the standard solutions contain only mercury ions, data shown in columns 4 and 6 should be equal. Results with acceptable relative standard deviations of ± 0.2 mg Hg(II) were obtained. Better precision would be possible if a sharper color shift corresponding to the first end point was visible (see the online material). The EDTA amount released from the Hg-EDTA complex is quantitative and reproducible.

Influence of Other Cations

Theoretically, the presence of the cations tested here is expected not to interfere with the mercury assay. However, secondary equilibria, other mixed-complex formation, or practical problems could not be discarded. Thus, the same experimental setup for determination of Hg(II) was repeated in presence of other common cations. An aliquot of 10.00 mL of a standard solution containing 30 mg Hg(II) was mixed with 1 mL of 0.01 M solutions of the following cations: Ca(II), Al(III), Mg(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Ba(II), Cr(III), and Fe(III). Then, the analytical titration was performed as described before. Volumes of zinc solution needed for the first end point were lower due to the increase of the total ions. The average and standard deviation of four determinations were 5.05 and 0.06 mL, respectively, but no differences in the mercury determinations were found between these determinations and those performed in absence of these foreign ions: mmol Hg found = 0.147 ± 0.002 , $n = 4$.

Table 3. Recovery Results of Mercury in Acidic Water Samples

Trial	147.7 μmol Hg(II) added		29.5 μmol Hg(II) added	
	Hg(II) Found/ μmol	Recovery (%)	Hg(II) Found/ μmol	Recovery (%)
1	145.2	98.3	28.9	97.8
2	154.3	104.0	28.8	97.5
3	145.2	98.3	28.3	95.8
4	151.3	102.4	28.3	95.8
5	148.2	100.0	28.9	97.8

Since Bi(III) is able to complex iodide ions to form stable compounds (see Figure 1), about 100 mg of Bi(III) (as carbonate salt) was dissolved in nitric acid and added to the standard Hg(II) solution. Analytical results obtained after EDTA addition and pH adjustment show no interference of this quantity of bismuth ions in the mercury content measurements.

Finally, the possible interference of ion Ag(I) was analyzed. This cation does not form a chelate with EDTA at pH 5.50. However, it could precipitate after addition of iodide ions. A few milligrams of AgNO_3 were mixed with the Hg(II) standard solution and a white suspension was observed in the yellow solution when iodide was added. At the end point, after the titration with the zinc standard solution, the suspension becomes purple. This distinguishable color change did not prevent accurate detection of the Zn(II)-xylenol orange complexation (see the colors in the online material).

Application to Battery Samples

The 100 mL aliquots of residual water from the bottles were analyzed by following the protocol for the standard solutions and no detectable amount of Hg(II) was found in any of the “real” samples. Negative results can be attributed to the short period of time used in this simulation of the leaching process or to the relatively high detection levels of the proposed method. As a consequence, these results *do not* imply that batteries can be disposed without any concern since the release of mercury would require much longer leaching times.

The recovery experiments at two Hg(II) levels carried out with the acidic water solution are shown in Table 3. The filtered solution was mixed with the buffer adjusted to pH 5.50, and indicator was added. The mixture was red before the addition of the excess of EDTA and turned yellow after the EDTA addition. Excellent recoveries were obtained for the higher amount of Hg(II) (147.7 μmol), but low results were achieved for the lower amount (29.5 μmol), close to the limits of detection of the method. At this level, the late perception of the first end point leads to an error in the first volume readings and, as a consequence, to negative errors in the Hg(II) recovery results.

Conclusions

This article describes a project proposed and performed at the end of the introductory course in analytical chemistry as part of the optional activities suggested to students. Two aspects can be highlighted. First, from these experiments, the students found an absence of mercury in the batteries exposed to water within the detection limits of this method. Second, these learning-lab activities, based on proposed projects, introduce important concepts and lab skills, and significantly increase the communication with the instructors. The students also have the opportunity to make decisions during their undergraduate career and to test out a complete project. Our experience suggests that activities of this kind offer a stimulating alternative to teaching science concepts and develops a greater interest in analytical chemistry science.

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