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## Qualitative Analysis of Antimony, Bismuth and Arsenic in Mixtures

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Cations of antimony, bismuth and arsenic react with potassium iodide and ether in presence of hydrochloric acid. The liquid reaction products can be hydrolysed and the three metal ions will accumulate in the third liquid phase which will form from the originally two phase system (ether-water).

The next step is to determine whether the obtained product consists of an individual liquid compound only or it is a binary or ternary mixture of the liquid compounds of the three cations in question.

In previous communications<sup>1,2,3</sup> the reactions of antimony, bismuth and arsenic with potassium iodide and ether in presence of hydrochloric acid were described.

The obtained liquid products can not be distinguished one from the other neither with regard to the colour nor to their consistence.

Those products are relatively stable only in the system in which they were formed. All the three products undergo degradation and hydrolysis in the air and in water respectively. In the air they decompose losing ether and leaving solid residues which in their appearance markedly differ one from the other. In contact with water products of hydrolysis were obtained which were specific for each of these cations (Table I).

The aim of the present investigation was to study whether mixtures of arsenic, antimony and bismuth could be differentiated by means of the above cited reaction, analysing the three reaction products after hydrolysis.

### EXPERIMENTAL

*Solutions.* The required amounts of arsenic trioxide, antimony trichloride and bismuth subcarbonate were weighed out and dissolved in 10, 15, 20 and 25% hydrochloric acid. Aliquots were removed from these stock solutions and mixed to make up the standard solutions 0.1 M in arsenic and antimony, arsenic and bismuth, antimony and bismuth, and arsenic, antimony and bismuth, respectively. These solutions were further diluted to be 0.05 M in individual components of the binary and 0.033 M of the ternary mixture.

*Reagents.* Saturated solution of potassium iodide in water, freshly prepared at room temperature, ether and hydrochloric acid. All chemicals used were reagent grade.

*Procedure.* The examined solution (4 ml) was agitated in a testing tube with potassium iodide solution (0.5—2 ml) and ether (2—3 ml) and then allowed to stand until the layers separated. Thereupon, a drop of the obtained liquid product is cautiously introduced by means of a pipette on the bottom of a Petri dish full of water.

TABLE I

*Degradation of the liquid products of antimony, bismuth and arsenic in air and in water*

Liquid product of	in air		in water	
	The droplet loses ether and leaves a solid residue		The surface of the droplet	The surface of the water — layer
Sb	transparent surface smooth	orange	opaque orange — yellow or red	film white yellow red
Bi	and bright	red then black	black	black brown red
As	opaque	orange — yellow	white	—

## RESULTS

Using potassium iodide and ether as reagents in presence of hydrochloric acid it is possible to demonstrate the presence of all the three cations, antimony, bismuth and arsenic, in a mixture. That can be accomplished because of the characteristic behaviour of the obtained liquid reaction product in contact with water.

Experiments have shown that arsenic can be distinguished from antimony and bismuth in mixture on the bases of the orange precipitate ( $\text{AsI}_3$ ), which is obtained on addition of potassium iodide, as well as on the bases of the subsequent formation of the white hydrolysis product ( $\text{As}_2\text{O}_3$ ) if the reaction is performed in solutions in about 10% hydrochloric acid or less. Antimony and bismuth could not be distinguished one from the other if both were present in the mixture.

The three cations however can be easily differentiated by means of hydrolysis because there is a preferential partial hydrolysis of the liquid compound of arsenic over that of antimony and bismuth in mixture. The liquid compound of arsenic hydrolyses at the most rapid rate, then follows hydrolysis of the product of antimony and finally that of the bismuth product.

In mixtures with antimony and bismuth arsenic could not be detected in the third phase when the concentration of hydrochloric acid was less than about 20%.

If a drop of the liquid product, containing either two or all the three components, i. e. the liquid product of antimony as well as that of bismuth and of arsenic, is introduced into water, a peculiar sequence of partial hydrolysis occurs. The reason for such a characteristic behaviour lies very probably in the differences in the rate of degradation of the individual liquid products in mixture.

The surface of the primary red and transparent drop becomes first white and opaque because of the hydrolysis of the liquid compound of arsenic. The white cover then breaks down and a yellow or red opaque one resulting from hydrolysis of the liquid product of antimony appears. Finally the surface of the drop turns black, the product of bismuth being the reason (Table II).

TABLE II  
*Degradation of the liquid product of mixtures of antimony, bismuth and arsenic in air and water*

Liquid product of	in air		in water	
			The surface of the droplet	The surface of the water — layer
Sb - Bi	transparent surface smooth and bright	orange red then black	orange-red then black	white yellow red brown black
As - Sb		orange yellow	white then orange-yellow	white yellow red
As - Bi	opaque	orange then black	opaque white then black	film black brown red
As-Sb-Bi		orange-yellow then black	white orange-red then black	yellow red brown black

The reaction with potassium iodide and ether in presence of hydrochloric acid can therefore serve, instead of an extraction process, to accumulate in a smaller volume antimony, bismuth and arsenic in form of the third liquid phase of the system, thus separating them from the water layer and ether.

On the other hand, the subsequent hydrolysis of the obtained liquid product serves as the differentiating test itself whether the product consists of an individual liquid compound only or is a binary or ternary mixture of the liquid compounds of those three cations. The observed characteristic sequence of partial hydrolysis of the components enables us to demonstrate the presence of either of the three cations in a mixture, the cations being thus temporarily separated one from the other.

The suggested differential technique can be divided into two procedures:

1. The reaction with potassium iodide and ether in presence of hydrochloric acid: synthesis of the liquid products, their accumulation and separation from the water layer and ether.

2. Differential analysis based on the hydrolysis of the obtained liquid product.

#### REFERENCES

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#### IZVOD

##### Kvalitativna analiza antimona, bizmuta i arsena u smjesi

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Razlikovanje antimona, bizmuta i arsena u smjesi uspjelo je provesti bez prethodnog odjeljivanja ovih kationa jednog od drugog, i to na temelju reakcije s kalijevim jodidom i eterom u nazočnosti klorovodične kiseline i potom hidrolizom dobivena tekućeg reakcijskog produkta. U tu svrhu stavi se kap dobivena tekućeg produkta, s pomoću pipete, na dno Petrijeve zdjelice napunjene vodom.

Opisanom reakcijom postizava se i akumuliranje navedenih triju kationa u manji volumen i njihovo odjeljivanje iz smjese kao posebne faze sistema.

Na temelju hidrolize dobivena tekućeg produkta moguće je zatim zaključiti, da li se radi o produktu antimona, bizmuta, ili arsena, ili o smjesi tekućih produkata pojedinih kationa. Najprije dolazi do hidrolize produkta arsena. Kapljica se prevuče čvrstim bjelim slojem arsenova trioksida. Zatim se nastala bijela čahurica rastvori, kasnije i otopi, a kapljica se obloži žutim ili crvenim čvrstim slojem produkta hidrolize antimona. Konačno se, nakon nekoga vremena, postepeno javlja krut crn sloj produkta razgradnje bizmuta.

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