

Remarks on the Decomposition of Orpiment and Realgar.

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For the decomposition of orpiment and realgar most workers advocate either *Nissen's* decomposition, on the action of sulphuric acid, or the dissolving of the sulphides with fuming nitric acid.

Sarudi (1) advocates fuming nitric acid for the decomposition in which case he adds a slight amount of tartaric acid to the decomposing solution with the purpose of keeping the minimum antimony oxides, which might possibly be present, in a dissolved state.

Biltz (2) advocates in his well known textbook *Nissen's* aforementioned method of decomposition.

Other workers (3), considering the fact that arsenic is, as it is separated by distillation from the antimony which it may contain, accomplish the decomposition directly in the distilling flask with nitric acid, finally expelling it with sulphuric acid.

Either method, either solution, is suitable and yields very good results, however, they can only be used to prepare the determination of how much arsenic the compound contains. On performing the decomposition by means of sulphuric acid, the decomposition already indicates that for the determination of the sulphur content a separate sample must be weighed out, furthermore on carrying out the decomposition with nitric acid or by *Lunge's* method, which would both be suitable for the determination of the arsenic content, as well as for that of sulphur, some loss of sulphur must always be taken into account, this loss is also mentioned by most authors.

Sarudi (1) has elaborated a method for the determination of sulphur. Accordingly, the very finely powdered sample is dissolved in concentrated sodium hydroxide, subsequently acidified with hydrochloric acid, evaporated to dryness, the residue is dissolved and the sulphate separated from the solution.

It can therefore be established that all investigators determine the sulphur amount from separately weighed samples.

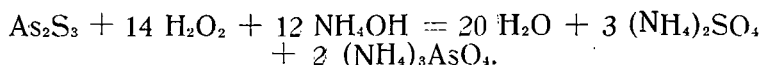
On performing mineral analyses the aim should always be to attempt to make the whole analysis exclusively on the base of one weighed sample. Based on the experiences gained in the course of the analytical examinations of minerals carried out at our institute, a method will be reported for the elimination of the aforementioned deficiencies and difficulties enabling the determination of the arsenic and sulphur content, in realgar and orpiment, in one weighing, without introducing large masses of foreign substances into the solution as occurred for instance in the previously mentioned case when concentrated sodium hydroxide solution was used for the dissolving.

The starting point was the analytical procedure which follows the usual decomposition on applying *Nissen's* method with sulphuric acid. In this case namely after the substance is completely dissolved and the insoluble residue filtered off, the arsenic is separated from the filtrate with sulphur hydrogen filtered, washed out with water containing hydrochloric acid and the precipitate consisting of

arsentrisulphide is removed from the filter through dissolving it with hot ammonium hydroxide (10%) containing hydrogen hyperoxide. The arsenic is then separated out from the filtrate obtained in this manner. Of course, the sulphur content must be determined by a separate weighing.

Obviously the assumption occurs that if the procedure described above can be accomplished with this precipitate, i. e. with artificially obtained arsentrisulphide, then the same solution is applicable to a naturally obtained, respectively naturally formed arsentrisulphide, thus orpiment can be dissolved without having been previously dissolved in sulphuric acid, and without the subsequent precipitation of sulphur hydrogen. This procedure enables on the one hand, the determination of the sulphur and arsenic content with one weighing and on the other hand it shortens the procedure significantly, as the decomposition with sulphuric acid, the precipitation with sulphur hydrogen, the filtration washing and redissolving (5) of the obtained sulphide precipitate are all eliminated.

Orpiment dissolves according to the known reaction described below:



For the decomposition the weighing of 0,05—0,1 gram quite sufficient. 20—25 ml 10% ammonium hydroxide and 5 ml 30% hydrogen hyperoxide is added to the extremely finely powdered substance to be decomposed. The beaker is covered with a watchglass to eliminate any loss caused by effervescence. The decomposition can be accelerated by gentle heating of the beaker through placing it, either on an asbestos wire-gauze over a small flame, or on the water-bath. When the effervescence ceases and the insoluble orpiment granules are no more visible on the bottom of the beaker, the excess hydrogen hyperoxide is destroyed, evaporated and diluted with 25—30 ml water on the water-bath, till the smell of ammoniak disappears, then it is filtered off and the insoluble residue on the filter paper well washed with hot water, and if only the aforementioned minimum amount had been weighed then the arsenic is directly determined and the sulphur is determined from its filtrate, if on the other hand a large amount was decomposed then stock solution is prepared.

With the application of this — as aforementioned — already previously known procedure which, however, has as yet not been used to dissolve, respectively to decompose orpiment and realgar, the desired aim is achieved, as after the filtration of the insoluble residue the solution only contains ammoniumarsenate and ammoniumsulphate and therefore one weighing is sufficient for the determination of both the arsenic and sulphur content.

The further determination of sulphate and arsenic exceeds the limits of this paper, nevertheless, for the sake of completion it should be mentioned that the most efficient manner is to separate out the arsenic in the form of magnesiumammoniumarsenate, according to the methods of *Winkler* (4) or *Sarudi* (6) and to repeat the separation

as described by these authors after having redissolved the precipitate filtered off the next day. The two filtrates are evaporated and a few drops of hydrochloric acid are added to the residue and it is dissolved again and evaporated, and finally it is dissolved and the sulphate amount is determined. The magnesiumammoniumarsenate precipitate which is separated for a second time is ignited into pyroarsenate and weighed.

Instead of gravimetric determination of arsenic, iodometric determination can also be applied. The arsenic is also separated out in the form of magnesiumammoniumarsenate (the precipitation is also repeated in this case), the precipitate on the filter is dissolved with hot N hydrochloric acid and the arsenic acid which is bound in the precipitate is iodometrically titrated in the solution according to the method of *Daubner* (7). Also in this case the sulphate is determined from the two filtrates of the magnesiumammoniumarsenate precipitates.

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Az auripigment és a realgár feltárására a legtöbb szerző vagy a Nissenon féle kénsavas feltárást alkalmazza, vagy pedig füstölgő salétromsavval oldja fel a szulfidokat. Az első esetben a feltárás természetéből következik, hogy a kén mennyiségét csak külön bemérésből lehet meghatározni, a füstölgő salétromsavas feltárásnál, pedig minden szerző egységes megállapítása, hogy minden esetben kénvesztéssel kell számolni. Olyan feltárára volna tehát szükség, melyből mind a két alkotórész, az arzén és a kén is meghatározható egymás mellett, anélkül, hogy az oldatban feltárás után idegen alkotórészek tömege volna jelen. Ismeretes folyamat, hogy az arzéntrisulfid ammoniumhidroxid és hidrogénhiperoxid hatására oldatba megy és ammoniumarzenát, valamint ammoniumsulfát keletkezik. Ezt a reakciót az ismeretes kénsavas feltárást követő analízisben már régebben is felhasználták, amennyiben a feltárás után az oldatból kénhidrogénnel leválasztották az arzént és az arzéntrisulfidból álló csapadékot leszűrve, a szűrőről ammoniumhidroxid és hidrogénhiperoxid elegyével oldották le. Ez a megoldás alkalmazható nemcsak a mesterséges úton kapott, hanem a természetes úton keletkezett arzéntrisulfid, tehát az auripigment oldására is. Ezen ismert reakciónak, az auripigment és realgár feloldására való felhasználásának előnye az, hogy az oldatban semmi idegen alkotórész nem kerül, csupán ammoniumarzenát és ammoniumsulfát jelenlétével kell számolnunk, mind az arzén, mind pedig a kéntartalom egy bemérésből meghatározható, végül a feltárás igen rövid időtartamú, amennyiben csak 5–6 percet vesz igénybe.