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Determination of the Level of Arsenic in Human Bodies (Population of Basle)*

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I. Introduction

Investigations of the normal arsenic level of the population of Basle have not been carried out till now. Nevertheless, despite the great reduction of arsenic poisonings, it is again and again necessary to consider arsenic intoxications in general, and especially those of a criminal nature. Therefore we have determined the arsenic level of various organs and parts of the body of 20 persons who died a sudden death in Basle of natural or accidental cause, or who committed suicide. At the same time these investigations were to serve as test of the suitability, in toxicological analyses, of the color reaction with silver diethyldithiocarbamate, which has recently been described in the literature for the quantitative determination of the minutest amounts of arsenic.

II. Micro-determination of Arsenic

Marsh published his pioneer attempts of micro-determination of arsenic as early as 1834 and 1837. He reduced the compounds of arsenic to arsine with hydrogen which was produced with zinc and sulphuric acid, and destilled off this volatile arsine in the flow of hydrogen. Arsine breaks down if strongly heated and metallic arsenic is formed, which is recognized in the form of an arsenic mirror. This method was later improved by various authors (Liebig, Lockemann). The method was involved and time consuming, and required a certain degree of experience.

Gutzeit, going forward from the basic idea of Marsh, proposed, in 1891, another simple method of determination of arsine. Certain heavy metal salts, applied to strips of paper, react with arsine to form colored compounds and thus can be used in determination of arsenic. The Gutzeit method — later modified by various authors — is today still the most frequently used method of demonstrating the presence of arsenic. However it has a number of disadvantages which can lead to errors:

1. The reproducibility of the colored spots depends on the development of hydrogen. An excessive of uneven flow of hydrogen causes irregular color spots.

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* Herrn Professor Berthold Mueller zum 70. Geburtstag zugeeignet.

2. A quantitative evaluation of the color spots is possible only visually. The intensity of the color decreases after a short time.

If these possible sources of error are born in mind, the Gutzeit method yields quite useful semi-quantitative results. Above all the method is simple and bears numerious possibilities of usefulness.

Recently a number of works have appeared which employ the color reaction of arsine with silver diethyldithiocarbamate for determinations.

VASAK and SEDIVE are the first to report the reagent silver diethyldithiocarbamate in the determination of arsenic. The procedure employs the same arsine generator as GUTZEIT, except that in place of the bell with reagent paper there is a U-shaped glass tube which conducts the flow of hydrogen into a test tube containing a solution of silver diethyldithiocarbamate in pyridine. The intensely yellow-colored solution turns slightly red when the arsine bubbles through it. The intensity of the color is finally measured quantitatively in a colorimeter.

A number of authors have used this new procedure on a great variety of materials. POWERS and co-workers used it for arsenic determination in petroleum oil, FRESENIUS described arsenic determinations in mineral waters, and JACKWERTH tried out the method with a view to its acceptance in pharmacopeias for arsenic determination in pharmaceuticals. Compared with the original Gutzeit procedure the method with silver diethyldithiocarbamate has the following advantages:

a) The absorption of arsine by the solution of silver diethyldithiocarbamate in pyridine is very rapid. Dependence on the strength of the flow of hydrogen is nullified, thereby achieving greater reproducibility of the values from analyses.

b) The color intensity is read in the colorimeter. The subjective influence of a visual reading is also nullified.

The interference of antimony is slight because the absorption maximum of its complex with silver diethyldithiocarbamate is different from that of arsenic.

The sensitivity of the reagent silver diethyldithiocarbamate lies between 0.1—20 micrograms of arsenic. This large range is very advantageous especially in determinations where the level of arsenic is unknown.

III. The Method Used

10 g of liver, 10 g of bone, 20 g of blood, and 30 g of urine were separately reduced to minerals by digestion with nitric and sulfuric acids. The residue was boiled off twice with water. All nitric acid must be removed since this interferes with the development of hydrogen and the reduction of compounds of arsenic.

The residue, free of organic material, is placed directly into the arsine generator with 10% sulfuric acid (Fig. 1).

A ml of very dilute copper sulfate solution and a small amount of stannous chloride solution were added. When these reagents were all in the generator flask, and a test tube of reagent, 0.5% silver diethyldithiocarbamate in pyridine in place, zinc was added, and the flask was tightly sealed at once. After 15 min the

10% sulfuric acid was partly exhausted. Then 10 ml of 20% sulfuric acid was quickly poured in and the flask resealed without delay. The apparatus was then left undisturbed for another 45 min.

The arsine passed through the yellow solution of silver diethyldithiocarbamate in pyridine forming a red complex. The now slightly red solution was finally measured in a Zeiss Elco II Colorimeter using the S 53 E filter and an absorption cell with a layer thickness of 1 cm. The sensititivity of the silver diethyldithiocarbamate, as seen from the calibration curve, is adequate for 0.2 μg, corresponding to an extinction of 0.008 (Fig. 2).

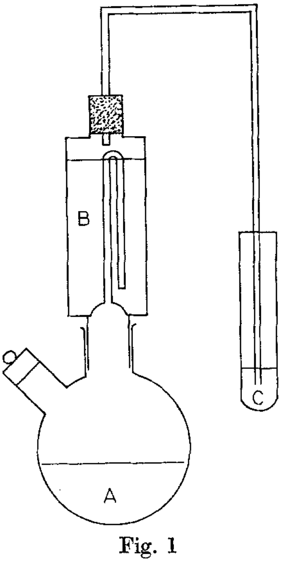

Fig. 1

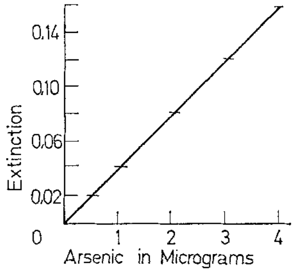

Fig. 2

Fig. 1. The arsine generator. The arsine generator as used with the silver diethyldithiocarbamate method. The solution "A" in the flask contains the minerals dissolved in sulfuric acid, plus zinc, copper sulfate, and stannous chloride. This mixture generates hydrogen and arsine. Solution "B" contains 5% cadmium acetate which removes hydrogen sulfide from the hydrogen and arsine as they pass through on the way to the color indicator. Solution "C" is the color indicator, silver diethyldithiocarbamate dissolved in pyridine. It absorbs arsine forming a red complex

Fig. 2. The Calibration curve. This was plotted using known quantities of arsenic. The degree of redenning of the color indicator was measured in a Zeiss Elco II Colorimeter. The reagent solution is used as the blank. As seen, the curve approximates a straight line, indicating that silver diethyldithiocarbamate turns red in direct proportion to the amount of arsine absorbed

IV. Results of the Analyses

In a number of persons who died in Basle we determined the arsenic level in liver and bone after autopsy. In several cases blood and urine were also done. The results of these analyses are shown in the table.

The autopsy numbers are those used by the Basle Institute of Forensic Medicine. The results are in terms of micrograms per hundred grams of tissue or urine.

Table. *The Results of Analyses*

Autopsy number	Cause of death	Arsenic in micrograms/100 g			
		Blood	Liver	Urine	Bone
148/64	suicide, hanging	—	1.5	—	6.0
149/64	traffic accident	—	2.0	—	1.3
150/64	suicide, Noludar	—	1.5	—	5.0
151/64	traffic accident	—	1.3	—	6.0
155/64	sudden death	—	1.3	—	3.0
159/64	traffic accident	—	2.0	8.3	8.0
160/64	autoerot. accident, strangul.	—	3.0	3.0	6.0
164/64	sudden death	—	2.5	—	1.6
166/64	autoerotic accident, hanging	—	1.3	1.0	10.0
80/65	sudden death	0.0	0.6	—	3.3
81/65	sudden death	0.6	0.1	—	0.0
82/65	suicide, Luminal	0.2	0.6	0.2	0.0
84/65	sudden death	0.4	1.3	—	1.1
85/65	suicide, hanging	0.4	1.5	—	0.0
86/65	sudden death	2.8	2.8	—	3.8
87/65	fall down stairs, accident	0.1	4.5	0.4	0.5
88/65	sudden death	0.6	0.8	—	0.3
89/65	sudden death	0.6	4.0	0.7	0.8
90/65	suicide, shooting	0.9	1.8	—	0.6
93/65	suicide, hanging	1.0	3.0	—	1.3

V. Discussion of the Results

The cadavers investigated in this research project were those of persons who died suddenly of natural or accidental causes in Basle.

The mean and maximal values we obtained, are as follows:

	Mean	Maximal
Blood	0.1 μg-%	2.8 μg-%
Liver	1.9 μg-%	4.5 μg-%
Urine	2.3 μg-%	8.3 μg-%
Bone	2.9 μg-%	10.0 μg-%

CURRY of England reports the following values:

Liver	1— 10 μg-%
Blood	0— 2 μg-%
Urine	1—100 μg-%

STEWART and STOLMAN of America report the following values:

Liver	3.5— 7.5 μg-%
Blood	2.6— 3.7 μg-%
Urine	3.1—32. μg-%

The tissue arsenic values obtained by us were therefore within the accepted norms and in fact were low normal on the whole. We have found that the relative tissue arsenic levels need not be similar in two different individuals. One individual might have high bone levels and low liver levels, whereas another might show the reverse relative levels.

Summary

Investigations of the normal arsenic level of the population of Basle have not been carried out till now. Nevertheless, despite the great reduction of arsenic poisonings, it is again and again necessary to consider arsenic intoxications in general, and especially those of a criminal nature. Therefore we have determined the arsenic level of various organs and parts of the body in a number of persons who had lived in Basle or its suburbs. At the same time these investigations were to serve as a test of the suitability, in toxicological analyses, of the color reaction with silver diethyldithiocarbamate, which has recently been described in the literature for the quantitative determination of the minutest amounts of arsenic.

Our autopsy material was obtained from 8 persons who died suddenly, from 6 who died in accidents, and from 6 who committed suicide by hanging, by shooting, or with barbiturates. The arsenic level was determined in liver and bone, and in some cases in blood and urine also. The values obtained were all under 10 µg-% (with one exception of 1a.0 µg-%) and therefore correspond to the lower limits of the normal vOlues given in the literature.

The color reaction with silver diethyldithiocarbamate has shown itself to be excellent for the determination of the minutest quantities of arsenic, and is especially suitable for routine determinations of arsenic in toxicological analyses.

Zusammenfassung

Die colorimetrische Arsenbestimmung mit Silberdiäthylcarbaminat erwies sich für forensische Untersuchungen als geeignet. Bei einem Kollektiv von Personen aus Basel, die an einem natürlichen oder unfallmäßigen Tod verstorben waren, wurde der Arsengehalt in verschiedenen Organen und Körperflüssigkeiten bestimmt. Die Durchschnittswerte an Arsen betragen für *Blut 0,1* µg-%, *Leber 1,9* µg-%, *Urin 2,3* µg-% und *Knochen 2,9* µg-%.

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