

## THE DETECTION OF POISONOUS METALS.

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THE object of this paper is to suggest methods for a rapid and simple qualitative search for poisonous metals. It is an advantage to limit the manipulatory operations as far as possible, rather than to test separate samples for special substances; and it is also most important to avoid the use of large quantities of reagents, involving risk of the introduction of adventitious impurities, and to be able to conveniently deal, if necessary, with quantities of organic matter as large as 4 or even 8 ounces.

For a preliminary analysis we therefore adopt the following two processes :

1. A Reinsch test for arsenic, antimony, bismuth, and mercury.
2. Extraction (without destruction of organic matter) by means of 50 per cent. nitric acid and a small proportion of sulphuric acid of lead, mercury, bismuth, copper, zinc, and chromium. By omitting the sulphuric acid, barium may also be here included.

As regards the Reinsch test, little need be said at present. We do not, naturally, claim for it the mathematical precision of the many excellent methods recently elaborated for the estimation of arsenic. It may, however, be well to mention a few of its advantages. It gives evidence of mercury, antimony, and bismuth, as well as of arsenic. It is a concentration method, permitting one to handle comparatively large amounts of substance in a reasonably short time, and thus enabling the analyst to obtain a sufficient amount of the poisonous metal to allow of its detection with added certainty. When seeking for traces, the material may be left to boil under a reflux condenser as long as desired. We consider the accuracy to be ample, having in numerous test experiments, which need not be described here, satisfied ourselves that 0.05 mgm. of arsenic may be recognised with absolute accuracy when added to as much as 8 ounces of visceral contents. With antimony satisfactory evidence is yielded by 0.1 mgm., but with mercury we find that really satisfactory evidence is not to be got with less than 1 mgm. in 4 ounces.

Having obtained a deposit on copper, the analyst has at his disposal numerous methods for further examination. We may, however, mention here that we find solution in pure sodium peroxide and a Marsh test the most suitable method for arsenic. We are, moreover, of the opinion that very little time is saved by a direct "Marshing" of the crude material. Although this latter process can be worked well with small quantities of material, we have not made any attempt to apply it to quantities of several ounces of substance having the varied characters of visceral ingesta.

In our second process nitric acid may be used alone, but we find that the addition of a small proportion of sulphuric acid improves the extraction of any metals that may be present. Exact data as to proportions are quoted in the tabular

comparison at the end of this paper. In general, we cover the material to be tested with 50 per cent. nitric acid, and add from 5 to 10 c.c. of concentrated sulphuric acid. The mixture is heated over a small flame in a dish to a pasty consistency, and the operation stopped when dense brown fumes are evolved—usually in less than twenty minutes. The residue is then suitably diluted and filtered. At this point lead may be sought for by means of sulphuric acid and alcohol; but, since calcium sulphate is often deposited, we consider it more reliable and quicker to detect lead in the following manner: The filtrate is rendered strongly alkaline with ammonia, and a slight excess of ammonium sulphide added. This precipitates phosphates, chromium hydroxide, and sulphides of iron, lead, mercury, copper, bismuth, and zinc, and on filtration and washing these are obtained practically free from organic matter. In this respect, and also in the certainty of precipitation, ammonium sulphide presents great advantages over the use of sulphuretted hydrogen in acid solution, where, as is well known, copious precipitates of organic matter are always obtained—for instance, in Autenrieth's process. In examining the precipitate we extract with dilute hydrochloric acid, which leaves copper and mercury. In this solution lead is searched for by sulphuretted hydrogen (which also, of course, precipitates bismuth), and confirmed as sulphate, and zinc is tested for after removal of lead, bismuth and iron, by ammonium sulphide. We do not find that it is necessary to carry out a phosphate separation before looking for zinc. Copper is extracted by nitric acid and confirmed with ammonia or ferrocyanide, and mercury is taken up with hydrochloric acid and potassium chlorate, and after evaporation tested for with stannous chloride.

By means of these two processes, from 4 to 8 ounces of material can be tested for all the metals named in from two to three hours with a minimum expenditure of reagents. The only method which appears to us at all capable of equally general application is that of destruction of organic matter by means of concentrated sulphuric acid, and we have therefore made a number of comparative tests, bearing on delicacy, expenditure of material, time involved, and bulk of solutions to be handled. We selected ground linseed cake as the experimental material, since it is homogeneous and contains more carbon than visceral contents; but as regards destruction by sulphuric acid, we think most analysts will share our opinion that 4 ounces of material is an excessive quantity with which to undertake this operation. We have tried large amounts, but in practice limit the quantity to not more than 50 grams.

Potassium sulphate, ammonium persulphate, and nitric acid have been used to facilitate the action, pure sulphuric acid being very much slower. The quantities of added metal have been reduced to amounts considerably short of what is likely to occur in practice, and we can only, therefore, make rough statements as to the qualitative evidence obtained. In every case there was added to the mixture 0.1 mgm. of lead, 0.2 mgm. of mercury, 0.6 mgm. of copper, and 1 mgm. of zinc.

The experimental material in cases 1 to 9 was powdered linseed cake, in 10 and 11 the stomach contents of a dog.

We think our results prove that the process of extraction with 50 per cent. nitric acid and a small proportion of sulphuric acid compares favourably with the

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destruction of organic matter in respect to time, delicacy, and expenditure of material. Ammonium persulphate is the best accelerator.

Material.	Reagent.	Time of Heating.	Vol. of Filtrate (Ammoniacal).	Lead.	Mercury.	Copper.	Zinc.
(1) 10 grams	50 c.c. $\text{H}_2\text{SO}_4$ 20 grs. $\text{K}_2\text{SO}_4$	6·45 hrs.	250 c.c.	Present	Doubtful	Present	Present
(2) 50 grams	300 c.c. $\text{H}_2\text{SO}_4$ 100 grs. $\text{K}_2\text{SO}_4$	6·45 hrs.	850 c.c.	Present	Absent	Present	Present
(3) 10 grams	60 c.c. $\text{H}_2\text{SO}_4$ 6 grs. $(\text{NH}_4)_2\text{S}_2\text{O}_8$	4 hrs.	250 c.c.	Present	Doubtful	Present	Present
(4) 50 grams	300 c.c. $\text{H}_2\text{SO}_4$ 85 grs. $(\text{NH}_4)_2\text{S}_2\text{O}_8$	7·25 hrs.	825 c.c.	Present	Doubtful	Present	Present
(5) 10 grams	50 c.c. $\text{H}_2\text{SO}_4$ 13 c.c. conc. $\text{HNO}_3$ added gradually	1 hr.	200 c.c.	Present	Absent	Not tested	Present
(6) 10 grams	40 c.c. $\text{HNO}_3$ 5 c.c. $\text{H}_2\text{SO}_4$	30 mins.	200 c.c.	Present	Present	Present	Absent
(7) 10 grams	40 c.c. $\text{HNO}_3$ 5 c.c. $\text{H}_2\text{SO}_4$	20 mins.	125 c.c.	Present	Doubtful	Present	Present
(8) 50 grams	150 c.c. $\text{HNO}_3$ 10 c.c. $\text{H}_2\text{SO}_4$	45 mins.	250 c.c.	Present	Present	Present	Present
(9) 10 grams	40 c.c. $\text{HNO}_3$ 2 grs. $(\text{NH}_4)_2\text{S}_2\text{O}_8$	20 mins.	100 c.c.	Present	Doubtful	Absent	Doubtful
(10) 15 grams	50 c.c. $\text{H}_2\text{SO}_4$ 20 grs. $\text{K}_2\text{SO}_4$	3·5 hrs.	225 c.c.	Present	Doubtful	Present	Absent
(11) 15 grams	40 c.c. $\text{HNO}_3$ 5 c.c. $\text{H}_2\text{SO}_4$	20 mins.	250 c.c.	Present	Doubtful	Present	Present

It may be of interest to mention the range of quantities actually found in the investigation of numerous cases of poisoning among animals. Reduced to milligrams per ounce they are :

Arsenic ...	...	...	...	...	...	5 to 0·3
Lead ...	...	...	...	...	...	140 to 15
Mercury ..	...	...	...	...	...	72 to 1·1

## DISCUSSION.

The CHAIRMAN (Mr. Fairley) asked whether in the Reinsch test the authors had any preference for copper gauze to foil. Some of the new remedies contained organic arsenic compounds—atoxyl, for instance—by means of which it was claimed that larger amounts of arsenic could be taken than in any other form. He did not quite see how such organic compounds would be dealt with in the authors' scheme, and he thought it would be necessary to first break up the organic combination. If the process suggested by the authors were relied on for the detection of mercury in a dilute nitric acid solution, it must be borne in mind that if there were present any sulphur compounds capable of producing mercuric sulphide, this was one of the most stable of the sulphides in the presence of nitric acid, and might not be decomposed.

But that, of course, only partially applied, because evidence as to the presence or absence of mercury would be afforded by the Reinsch test.

Mr. F. W. RICHARDSON asked how the authors' procedure would apply in the case of beer. As far as the detection of arsenic in beer or in human remains was concerned, he could not altogether accept the authors' suggestions. Some years ago (*Journ. Soc. Chem. Ind.*, 1902, **21**, 901) he had recommended oxidation of the organic matter with nitric acid and sulphuric acid in a flask, the flask being connected with a Woulffe's bottle containing a considerable quantity of water, into which the nitric and nitrous acid gases were drawn and absorbed. By that method, which he still used constantly, human remains could be readily oxidised, and beer completely. Then, by the Gutzeit test, as little as  $\frac{1}{1000}$  mgm. of arsenic could be detected in 70 c.c. of liquid, and at the end of the experiment a purely mineral solution was obtained which could be used for the ordinary processes of examination for other metals. His experience of the Reinsch test, which he had tried several years ago, was that it was of very little use for the detection of minute quantities of arsenic.

Mr. CHAPMAN, referring to Mr. Richardson's remarks, said that in testing for arsenic it was quite unnecessary to destroy the organic matter save in a very few cases, seeing that perfectly accurate results could be obtained by introducing the organic solution directly into the generation flasks. His own experience in this direction had been very considerable, and had been amply confirmed by the experience of many of his colleagues. He agreed with Mr. Richardson that the Gutzeit test was capable of detecting with certainty minute quantities of arsenic, but, whilst it was rapid and convenient, it possessed several serious disadvantages as compared with the Marsh-Berzelius process. He should have thought, however, that the detection of exceedingly minute quantities of arsenic was rather outside the subject-matter of the present paper. For the destruction of organic matter prior to an examination for poisonous metal, he (Mr. Chapman) had often found it a great advantage to oxidise with strong sulphuric acid in a manner similar to that observed in the ordinary Kjeldahl method. In this way, mercury and other metals which were volatilised on ignition could easily be obtained in a condition suitable for the application of the ordinary analytical procedure. He (Mr. Chapman) had had a great deal of experience of the Reinsch test, and could confirm the author's observation that positive results could be obtained with arsenic acid, but this was probably due to the fact that the hydrochloric acid in the presence of organic matter reduced the arsenic acid to the arsenious condition.

Mr. P. A. E. RICHARDS said that the sulphuric acid process mentioned by Mr. Chapman was, in his experience, a very good one. With regard to the detection of tin in stomach contents, etc., if a small piece of zinc were placed in the slightly acid fluid a deposit of tin would be obtained on it which could be easily and speedily dissolved by boiling with strong hydrochloric acid. The usual tests could then be applied to this solution.

Dr. LANDER, in reply, said that he should object on practical grounds to what he might call the "mathematical" detection of a metal-like arsenic, which, from a purely practical standpoint, was not a desideratum. Personally he preferred foil to

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gauze in the Reinsch test, because on a small surface the deposit was more concentrated. He had had no direct experience with atoxyl, but thought it probable that it would be decomposed by boiling hydrochloric acid of the strength used. But since atoxyl was not a poison, it would perhaps be an advantage if it did not give a deposit on copper. He was obliged to the Chairman for his suggestion as to the possibility of mercury being overlooked through non-decomposition of the sulphide. It was certainly important to bear this in mind. He agreed that the method of oxidation with sulphuric acid and nitric acid was excellent for the complete destruction of organic matter, but in looking for small quantities of lead, copper, zinc, and so on, large quantities of material must be operated upon, and this tedious destruction was what they had tried to avoid. They had tried some of the electrolytic methods, but had not obtained particularly good results with them. Tin, as had been mentioned, was not included in their scheme, but he agreed with Mr. Richards that in quantities likely to be dangerous it would be readily detected by deposition on zinc.

