

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

OSMIUM TETROXIDE POISONING.

I HAVE been unable to find any record of fatal cases due to exposure to the fumes of osmium tetroxide, but indirectly one case of fatal poisoning has come to my notice. This case was referred to by Mr. C. M. Hoke in an article appearing in the *Jewelers' Circular*. My interest lies particularly in determining the pathology both of the acute condition and of chronic poisoning, with the expectation of subsequently developing some method of neutralising the effects.

It may not be generally known that inhaling the fumes of osmium tetroxide in high concentration is a very dangerous procedure; and, if the effect on human beings is at all analogous to that on experimental animals, it would seem probable that some cases of fatal poisoning must have occurred in the past. In animals, at least, the cause of death is a pneumonia which appears very shortly after their exposure to the fumes.

Any information that can be given me in this connection will be deeply appreciated.

F. R. BRUNOT.

U.S. PUBLIC HEALTH SERVICE,
WASHINGTON, U.S.A.

THE POSSIBLE EFFECT OF SULPHUR DIOXIDE WHEN USED AS A PRESERVATIVE FOR DRIED FRUITS, ETC.

IN the course of routine work on products preserved with sulphur dioxide, and more particularly with fruit juices, the presence of hydrogen sulphide has made itself evident to the users by its odour and the flavour of the juices after dilution.

Under some conditions the presence of hydrogen sulphide was suspected in dried fruits also, and it was in connection with the examination of some hundreds of such samples that the following information was gathered.

For the prevention of the growth of moulds and the elimination of living organisms, it is necessary to "sulphur" such fruits as raisins, sultanas, apricots, peaches, apples and pears before they are marketed, and, for the preservation of fruit juices, either sulphur dioxide or benzoic acid may be employed.

In the course of work undertaken in Spain, France, Italy and Greece, I have been able to reduce the proportions of sulphur dioxide to a minimum without diminishing the market value or keeping qualities of the dried fruits, but the moist pulps need different treatment, and the existing Regulations permit the use of larger proportions. It is in these products, which are used for the preparations of syrups and "soft" drinks, that the effect of sulphur dioxide is most pronounced.

In order to demonstrate the possible state or situation of the sulphur dioxide in dried fruits, the following examination was made of a shipment of sultanias:

Sulphur dioxide before washing	..	375	parts per million.
„ „ after washing	..	320	„ „ „
„ „ in the washings	..	45	„ „ „

This seems to indicate plainly that most of the gas is present as an actual compound of the aldoses with the sulphite.

It might be argued that such a compound was entirely harmless to consumers of such fruit, but such a contention would not hold good if the dried fruit were used for making, say, artificial wines, mince meat or sauces, and the same disability is attached to the use of fruit pulps containing sulphite, either added purposely or left in barrels accidentally after cleaning, for I have found that a yeast fermentation becomes possible in diluted solutions; and, when that is active, the sulphur compounds are reduced to hydrogen sulphide.

To prove that this was possible, I expressed the juice from some Almeria grapes, sterilised it by boiling, and divided it up in flasks. To one, sulphur dioxide was added in the form of sodium bisulphite to approximately the proportion of 750 parts per million, as permitted in the Regulations. To another nothing was added. Both were then inoculated with a platinum wire dipped in an active growth of yeast. Other flasks were used as controls, and the neck of each was covered with a piece of lead paper and an inverted beaker.

After 24 hours at 65° F. an active fermentation was set up in the plain juice, but nothing had commenced in those containing sulphur dioxide. These were then diluted with more sterilised juice and left for several days under the same conditions, the results being as follows:

Flasks, to which no sulphur dioxide had been added, produced no coloration whatever on the lead paper, but with those containing the diminished proportion of sulphur dioxide, active fermentation had started, and the lead papers were marked with a perfectly defined black disc on an unstained white background.

Some difficulty was experienced in obtaining dried fruit free from sulphur dioxide for similar tests, but such samples as I have tested and found free from it yield no blackening whatever with lead paper when they are suitably mixed with water and fermented.

A fermentation test for the presence of sulphur dioxide, is too complicated for routine work, but I found that "sulphured" fruit and "sulphited" pulps have the disability that, when moistened or diluted with syrup, they develop an objectionable amount of hydrogen sulphide if once fermentation by yeast is allowed to commence.

It is necessary, therefore, to prevent the possibility of conditions which will permit fermentation, and, among other precautions, such products should be examined for the presence of active yeast cells; and if such are found present, the syrups or mixtures should be pasteurised before bottling.

C. EDWARD SAGE.

ANALYTICAL LABORATORIES,
10, LONDON STREET, E.C.3.

THE DETERMINATION OF PHOSPHORUS IN STEEL, ALLOY STEELS AND CAST IRON.

MR. ETHERIDGE, in his paper on "The Determination of Phosphorus in Steel, etc." (ANALYST, 1931, 14), begins by remarking that "Phosphorus is oxidised to ortho-phosphoric acid in nitric acid solution," and on page 16 he remarks that "oxidation

with permanganate is necessary to destroy organic matter. . . . The omission of permanganate leads to low results, possibly due to the interference of organic substances. . . .”

My own experience has led me to confirm the experience of others, that phosphorus is not completely oxidised to orthophosphoric acid when steel or iron is dissolved in *dilute* nitric acid, and that the addition of potassium permanganate is made for the main purpose of converting the phosphorus into orthophosphoric acid; the oxidation of carbonaceous matter is of decidedly secondary importance. Carbonaceous matter may be oxidised by means of several other oxidising agents, but very few of them will convert the phosphorus into orthophosphoric acid.

If a mild steel with very little carbon, but, say, 0.1 per cent. of phosphorus, is dissolved in dilute nitric acid, it will be found that, although there is little or no carbonaceous matter present, the precipitation of the phosphorus will be seriously low without the addition of permanganate, thus illustrating my point that the function of the permanganate is primarily to convert the phosphorus into orthophosphate. It may be mentioned, however, that if a steel is dissolved in dilute nitric acid or *aqua regia*, the complete conversion of the phosphorus into orthophosphoric acid will take place if the solution is evaporated and the residue baked.

Another interesting fact is that, so far back as 1885, J. Mackintosh showed that phosphorus in a solution of steel in hydrochloric acid may be oxidised to orthophosphoric acid by means of a stream of sulphur dioxide gas without oxidising the ferrous iron.

On page 16, Mr. Etheridge remarks that “it would be possible to add ammonium nitrate at this stage, but this would require less nitric acid to be used in dissolving the steel, which would be undesirable for rapid solution and oxidation of the carbides formed.” He may be interested to know that in the “Analoid” method for phosphorus in steel, 2 grms. of drillings are dissolved in no more than 30 c.c. of nitric acid (sp. gr. 1.20), that solution takes place very quickly, and there is no difficulty with regard to oxidation of the carbides formed. Thousands of tests which have been made by works’ chemists by this method over a period of ten years or so, support this statement.

On page 18, the author refers to my paper on the effect of titanium on the determination of phosphorus, but goes on to say that “It is fortunate that it is not usual to encounter low-phosphorus iron with much more than 0.01 per cent. of titanium.” If, however, he refers to p. 111 of *The Proceedings of The Cleveland Institution of Engineers*, 1919–20, he will see that I have analysed 16 definite brands of pig iron from different parts of Great Britain, and that the titanium in these ranged from 0.08 to 0.42 per cent., the average being about 0.15 per cent. One feature of my paper was to show that most haematite pig irons contain a moderate amount of titanium, which calls for attention in the determination of phosphorus.

On p. 20, the author refers to vanadium and tungsten steels, and states that in tool steels with 15 per cent. of tungsten some of the tungsten is precipitated, and that this always carries down some phosphorus. It may be mentioned, however, that in a process which I have worked out, good results are obtained by dissolving the steel in nitric acid, followed by a liberal supply of potassium permanganate. This method, which has been in use for some ten years, was given in detail in the *J. Iron & Steel Inst.* (1926, No. 1, p. 464).

The reference to Messrs. Rooney & Clarke’s paper, given on page 21 of *THE ANALYST*, contains a misprint—the year should be 1926, not 1925.

Taken as a whole, however, Mr. Etheridge's paper contains much useful information, and these remarks are not intended in any way to detract from its value.

N. D. RIDSDALE.

LABORATORY, 3, WILSON STREET,
MIDDLESBROUGH.

WITH reference to Mr. Ridsdale's remarks on the use of potassium permanganate, while there is no doubt that low results are obtained if it is not used, the mechanism of its action is not clear. Most authorities consider that meta-phosphoric acid is formed, and that potassium permanganate assists in transforming this into ortho-phosphoric acid. In both acids the phosphorus is fully oxidised, and the transformation of meta-acid into ortho-acid is a hydration effect, not oxidation, hence the difficulty of explaining why permanganate is necessary. According to the text-books meta-phosphoric acid is quickly transformed into ortho-phosphoric acid by boiling in the presence of mineral acids, but this is retarded by organic acids. It is possible, therefore, that the permanganate, by destroying these acids formed from the carbon of the steel, may thus indirectly assist in the transformation of meta- to ortho-acid.

Dr. B. S. Evans has recently carried out some experiments which appear to show that phosphorous acid is formed on dissolving steel in nitric acid, and he has further found that dilute nitric acid has practically no oxidising action on phosphorous acid. Bauer and Deiss (*Sampling and Analysis of Iron and Steel*) also state that phosphorous acid is formed. Brearley and Ibbotson (*Analysis of Steel Works' Materials*) state that phosphorus in steel is not completely oxidised by nitric acid alone. It seems probable that phosphorous acid is formed in the first place and partly oxidised to phosphoric acid by oxides of nitrogen produced by dissolving the steel in nitric acid, but it is necessary to complete the conversion to phosphoric acid with an energetic oxidiser such as potassium permanganate. Dr. Evans has also shown that chromic acid is not a sufficiently powerful oxidiser in this case, having little or no action on phosphorous acid.

As regards the use of a smaller amount of nitric acid than is specified in the paper, while 30 c.c. would be satisfactory in many cases, there are alloy steels which deposit carbides which are difficult to dissipate, and for these an excess of nitric acid is an advantage.

My experience with haematite cast iron is, no doubt, considerably less than Mr. Ridsdale's, but I have not encountered any with more than traces of titanium.

With regard to Mr. Ridsdale's method for high tungsten steels, in which tungsten is held in solution by using less nitric acid throughout, it is admitted that tungstic acid is liable to separate, to some extent, in the later stages, and phosphorus must be recovered from this precipitate, as was pointed out by Rooney and Clarke (*J. Iron and Steel Inst.*, No. I, p. 466). Furthermore, the lower acidity favours co-precipitation of arsenic, which may demand a reprecipitation. Also, it is by no means safe to use the same values for the volumetric solutions unless they are standardised under the same conditions, as the precipitate of ammonium phosphomolybdate does not appear to be quite in accordance with the formula when precipitated from solutions containing only a small excess of nitric acid.

I wish to thank Mr. Ridsdale for his interesting comments.

ARTHUR T. ETHERIDGE.

RESEARCH DEPARTMENT,
ROYAL ARSENAL, WOOLWICH, S.E.18.