THE USE OF BARIUM PEROXIDE IN THE ESTIMATION OF TOTAL SULPHUR IN URINE

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Although the Asbóth-Modrakowski method gives the best results for the estimation of total sulphur in urine (see preceding paper), it has the disadvantage of being somewhat lengthy. In metabolic experiments, where it is necessary to make a large number of estimations, it is essential that a process should be adopted which can be carried out rapidly. From this point of view the Pringsheim method seemed to be the best, provided it could be modified so as to give figures equal to those obtained by the Asbóth-Modrakowski method. With this end in view it occurred to me that the use of barium peroxide, in the fusion of which a higher temperature is obtained than with sodium peroxide, might lead to a more complete oxidation. The introduction of a barium salt would have the additional advantage of shortening the method, as the barium sulphate is formed during the actual process of the oxidation.¹ I therefore tried fusing with barium peroxide instead of sodium peroxide, but found that fusion did not take place easily.

This difficulty was overcome by the addition of sodium peroxide to the barium peroxide in the proportion of seven to one. The process was then carried out exactly as in the Pringsheim method, the details of this new method being as follows:—

1. Applying this idea to the Kongschegg method, I found that the addition of barium nitrate does not give any better results than when it is absent. The following are my mean figures, given in grammes of sulphur per 10 c.c. urine:—

Method	Urine A	Urine B	Urine C	Urine D
Kongschegg	0.0104	0.0104	0.0145	0.0045
Barium-nitrate-nitric acid ...	0.0102	0.0109	0.0144	0.0042

The addition of barium peroxide in the Asbóth-Modrakowski method did not yield concordant results, and as the method is too lengthy I did not pursue it further.

In the literature the only references I could find with regard to the utilisation of a barium salt in the estimation of sulphur were:—

(a) H. Weidenbusch, who, at Liebig's suggestion, estimated sulphur in albuminous materials by fusing a paste formed of the substance, barium nitrate and nitric acid. He gives no control analyses. *Liebig's Ann.*, Bd. LXI, S. 370, 1847.

(b) Alb. Edinger used barium peroxide to estimate sulphur in inorganic and organic substances, finally fusing with sodium peroxide. *Zeitsch. f. analyt. Chem.*, Bd. XXXIV, S. 366, 1895.

Ten c.c. of urine were measured into a nickelled steel crucible, as recommended by Pringsheim,¹ and made alkaline with sodium carbonate. After the addition of 0.4 grm. lactose, the mixture was evaporated down, on the water-bath, to a syrupy residue. Without further drying, the residue was carefully mixed with 8 grms. of the oxidising agent, consisting of 7 grms. of sodium peroxide and 1 grm. of barium peroxide.²

The crucible is next immersed up to three-quarters of its height in distilled water contained in a larger porcelain crucible or basin. A red-hot iron nail is introduced through the hole in the lid, and in a few seconds the reaction is completed. When the crucible has cooled down sufficiently it is overturned into the water, the basin being covered by a clock glass. The contents of the basin are then transferred quantitatively into a 500 c.c. Erlenmeyer flask and raised to boiling point. Concentrated hydrochloric acid is added gradually to the boiling fluid until the ferric oxide (derived from the iron nail) has gone into solution. A small excess of hydrochloric acid and a few c.c. of alcohol are then added, and the boiling continued for a short time. This serves to drive off the chlorine, which is always formed by the action of the excess of sodium peroxide on acidifying the solution with hydrochloric acid. It was noticed that under the above conditions the oxidation (as judged by the absence of carbonaceous particles) is complete, whilst without the use of barium peroxide filtration is very frequently essential in order to remove particles of carbon. The barium sulphate which is now present in the form of a granular precipitate is then collected on a weighed Gooch crucible, dried, ignited, and weighed as usual. It was found as a further advantage of the barium peroxide addition that the barium sulphate precipitate settles and filters very easily, probably owing to the physical conditions under which it is formed.

Using this method my analytical figures were the following:—

URINE B

10 c.c. urine gave	0.0857 gr. BaSO ₄	=	0.0118 gr. sulphur	in 10 c.c. urine
" " "	0.0837	"	= 0.0115	" " "

URINE C

10 c.c. urine gave	0.1112 gr. BaSO ₄	=	0.0153 gr. sulphur	in 10 c.c. urine
" " "	0.1122	"	= 0.0154	" " "

1. The crucible, together with the perforated lid, is obtainable from Messrs. Köhler, Leipzig.

2. A certain amount of care must be exercised in the addition of the oxidising agent. I found it advisable to add about 0.1 to 0.2 gramme at a time at the beginning. After the addition of about half the required amount, the remainder may be added in larger quantities. The barium peroxide used was tested for sulphur with negative results.

URINE D

10 c.c. urine gave 0.0472 gr. BaSO_4 = 0.0065 gr. sulphur in 10 c.c. urine
 „ „ „ 0.0488 „ = 0.0067 „ „ „

From this it will be seen that the results agree well *inter se*. If we compare the mean figures obtained by this method with those obtained without the use of barium peroxide (Pringsheim method) it will be seen to give considerably higher results. Compared with the Asbóth-Modrakowski method the results are a little higher, showing that under these conditions the oxidation is even more complete than in the Asbóth-Modrakowski method.

			Urine B	Urine C	Urine D
Pringsheim method	...	...	0.0110	0.0143	0.0044
Asbóth-Modrakowski method	...	...	0.0113	0.0152	0.0053
New method	...	...	0.0117	0.0154	0.0066

It follows, therefore, that the estimation of total sulphur in urine by means of a mixture of barium and sodium peroxides gives the highest results and possesses the further advantage of being carried out rapidly.

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