

## REFERENCES

- <sup>1</sup> J. Agterdenbos and N. Martinius, *Talanta*, 1964, **11**, 878.
- <sup>2</sup> J. E. Barney, II and R. J. Bertolacini, paper presented at the Eighth Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1957.
- <sup>3</sup> J. E. Barney, II and R. J. Bertolacini, *Analyt. Chem.*, 1958, **30**, 202.
- <sup>4</sup> R. W. Klipp and J. E. Barney, II, *ibid.*, 1959, **31**, 596.

SIR,

When we saw Dr. Barney's letter<sup>1</sup> we were appreciative that he, who should be a specialist in this respect because he was the first investigator who applied barium chloranilate to the determination of small amounts of sulphate, had read our paper<sup>2</sup> and given some comments on our work. After we had read his letter, however, it seemed useful for us to reply to his comments.

1. Dr. Barney suggests that the results of our calculations are so self-evident that it is unnecessary to publish them. We cannot agree with this view. Of course, qualitatively, they are self-evident, but they are so in many analytical determinations where equilibria play an important role. Fortunately, however, the magnitude of the effect is not large enough in many cases to cause a significant change of the calibration curve from linearity and significant influence of ionic strength on the curve. In the problem we studied, the magnitude of the deviations proved to be sufficiently large to be discussed quantitatively. We believe that our calculations give a good insight into the scope and limitations of the method. We are afraid that some error is involved in Dr. Barney's statement that some figures from his references 3 and 4 give information on the calibration curves he obtained. We regret that we could not find any information of the kind suggested in these references. (Unfortunately no report was available of the lecture. From the footnote to his paper in reference 3 and from our reference 1 in this letter we conclude, however, that his reference 3 should be regarded largely as a written report of this lecture.)
2. Dr. Barney's conclusions on the error made in the determination of the blank values in our Table IV are not well founded for at least two reasons. Firstly, he makes his conclusions from the values found in our Fig. 2. However, the experiments made to obtain the values in this figure were much more complicated than those used to obtain the values of Table IV. Secondly, the value of 0.04 he gives for the error in the absorbance is rather pessimistic. Our Fig. 2 clearly shows that the range found at the highest concentration level is about 0.05 or 0.06 extinction unit, obtained from 6 or 7 determinations. This gives a most probable value of about 0.02 for the value of the standard deviation. An error of 0.04 may, of course, be found, but it may be expected only in a few cases, even in the more complicated experiments.
3. We cannot agree with Dr. Barney's conclusions on the preparation of the reagent. The fact that we did not obtain satisfactory results when it was prepared according to Dr. Barney's directions (with a large excess of barium) may arise from slight differences in the preparation procedure. Without further experimental evidence, however, we cannot see that our procedure (using a small excess of chloranilate) should surely give rise to less satisfactory results than Dr. Barney's procedure, because an excess of barium may give inconsistently low results. In fact, our investigation included a large variation in the amount of reagent used for determination of the blank. No influence of such a variation on the blank value was found and it was, therefore, concluded that the contamination of our reagent was not important. Dr. Barney's conclusions on the value of our blanks are badly founded by his comparison with his own values, because we clearly showed the influence of alcohol concentration and ionic strength and both were quite different in his and in our experiments. In fact, our value was about 0.88 in a 4-cm cell, which seems favourable when compared with his value of at least 0.6 in a 1-cm cell!
4. Regarding the use of urotropine, we prefer the use of this buffer to acetate because it may be assumed that under our experimental conditions it has a lower ionic strength at the same buffering capacity.
5. From the values we cited for the dissociation constants of chloranilic acid in water ( $pK_1 = 0.85$ ,  $pK_2 = 3.18$ ), it follows that no significant contribution of the acid chloranilate may be expected in this solvent at about pH 5.2. It is difficult to predict the apparent pH required to fulfil this condition in about 70% alcohol, but the fact that a small change in apparent pH did not influence the value of  $\epsilon$  (page 881 of our paper) makes it probable that no significant amount of acid chloranilate were present in our experiments.
6. Dr. Barney suggests that the results of our Table IV should show the effect of ionic strength on the error. However, it should be clear from both this table and page 882 that it only gives the

relationship between ionic strength and extinction. The values given indicate that theory and experiment agree well, and Table IV on page 881 gives the information which Dr. Barney wishes for some practical conditions!

7. We do not believe that in practice the problem of the determination of small amounts of sulphate is restricted to samples with low and well known ionic composition. We cannot, therefore, agree with his conclusion on the usefulness of the method. In samples with favourable ionic composition, however, the method is useful (as we said on page 884 of our paper).

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<sup>2</sup> J. Agterdenbos and N. Martinus, *ibid.*, 1964, **11**, 875.

#### Concerning a certain international experiment

SIR,

In a paper by Cook *et al.*, which appeared in this journal,<sup>1</sup> results were given of an international comparison of analytical methods, designed to show the accuracy and precision of some techniques of routine trace analysis for nuclear materials. This interesting and, in its way, original work was arranged in order to compare the analytical results of some relatively common materials (aqueous solutions containing the nitrate salts of copper, chromium, manganese and mercury), obtained by four different methods in nine representative laboratories in various countries. The extensive and important material accumulated during the investigation has been subjected by the authors to an elementary statistical treatment:<sup>2</sup> in particular, mean values were calculated, also standard deviations and confidence limits of single determinations and of the average results; all this data was presented in the paper as tables and figures. The reduced data shows clearly that some of the methods compared are preferable from the point of view of precision and accuracy. In this way, the importance of the work carried out by the co-operation of international research workers is obvious and has been pointed out more than once<sup>3,4</sup> in reviews.

However, in our opinion, the method chosen by the authors<sup>1</sup> of presenting the results of the research is not the best, because the points of many important conclusions of the work are not made or remain obscure. It is necessary to point out separately that the vast experimental material accumulated by the international researches (551 results in all) could serve as a source of far greater extent and variety of information (or international interest!), than the information which the reader can find in the paper in question. In particular, it does not seem to be quite correct to incorporate results (for their subsequent statistical treatment), some of which may possibly not appertain to the same population. Besides, when dealing with samples of analysed results of different sizes ( $n$ ) and different origins, it seems that for the sake of clarity the values of standards ( $s$ ) should be given rather than confidence limits ( $ts$ ), *etc.*

Most probably in the treatment of such statistical material a multifactor analysis of variance would be very useful.<sup>5-12</sup> Such mathematical treatment would allow the clear revelation of errors of repeatability and reproducibility, as well as errors which are inherent in the different methods within the same technique, *etc.* Also, it would be useful to clear up these questions whether the accumulated results are submitted to the law of normal distribution, or whether they are to fulfil some other statistical procedure for "squeezing out" the maximum information from the results.

Undoubtedly, it would hardly be possible for each reader to present his own "account" to the authors and to satisfy all claims of this type. That is why we should not judge the authors severely and this is not the purpose of our letter. Slips are almost inevitable in any new matter, and to criticise is always somewhat easier than to do the job.

We consider it expedient that the authors of the article refer to the accumulated material once more and publish it in this journal as tables of all (without exception) initial numerical data. This would allow the specialist, possessing different methods of statistical treatment of experimental results and having different interests, to treat the material according to his own judgement—*lege artis*—and to extract for himself the maximum use of the information. We clearly recognise that these deliberations are rather late, but nevertheless "Better late than never!" Briefly: *Numerus fundamentum rei publicae.*