

NITRATES AND NITRITES (II).

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IN my previous paper on this subject (ANALYST, March, 1887) I showed only that a fair agreement existed between the total nitrogen and the conjoined estimations of nitrates and nitrites. My present aim is to prove that the method gives absolutely accurate results.

In my early experiments, the results were far from uniform, owing to the extraordinary delicacy of the naphthylamine test. The source of error lay in the water used. It was necessary to prepare water absolutely free from nitrogen. To do this it is best to treat it with a copper-zinc couple for *at least* a week, render alkaline, and distil slowly, rejecting that portion containing ammonia. Ordinary distilled water gives a strong colouration with the naphthylamine. I believe the nitrous acid is chiefly the result of oxidation of the ammonia, which all distilled water contains.

After eliminating all sources of error, I found that the determination of nitrates and nitrites when known quantities were added to *pure* water agreed absolutely with the colours produced for comparison by known quantities of the salts used separately. For instance: A litre of nitrogen-free water has added to it 5.0 mg. N in the form of KNO_3 , and .3 mg. N as KNO_2 .

100 c.c. is evaporated to dryness for nitrates, and the colour produced by the phenolsulphonic acid test is identical with that yielded by .5 mg. N similarly treated. Hence 1 litre = 5.0 mg.

Again, 100 c.c. are tested for nitrites, and the colour is copied by .03 mg. N = .3 mg. per litre.

In applying the naphthylamine test, it is necessary that the solution of naphthylamine hydrochlorate should be colourless, or nearly so. The colouration developed by standing is easily removed by animal charcoal. It is a good plan to keep charcoal in the solution, the supernatant liquid can be taken up by a small pipette, from which the drop or drops is added to the water under examination.

Similar quantities of the reagents must be used in each tube. This is especially necessary in determining nitrates. Different *shades* (not depths) of colour may be produced if attention is not paid to this point. I find the most trustworthy method is to evaporate *just* to dryness, or just short of dryness, add ten drops phenolsulphonic acid from a small (1 c.c.) pipette, agitate, add 1 c.c. water, and three drops strong sulphuric acid, then dilute, add ammonia in excess, and make up to 100 c.c.

The naphthylamine test is far superior to metaphenylene diamine for ascertaining when all nitrites are reduced by the copper-zinc couple, and its use has led me to the opinion that the surface of zinc recommended by the water committee, viz., 3×2 inches, is insufficient for the purpose; that is, if one desires the reduction to be completed in twenty-hours. Using that amount of zinc in 100 c.c. of water of 42° of hardness led to the following:—

					N per litre.	Naph. test.
In 24 hours	1.03	Red
„ 3 days	1.71	„
„ 4 „	2.04	„

It was then kept at 80°F. for a whole day.

In 7 days 3.71 None

Again. (1) 50 c.c. of standard potassic nitrate solution was made up to 500 c.c. with this same hard water; the total nitrogen expressed as ammonia being 10.1412 milligrammes.

(2) 50 c.c. of potassic nitrate solution was diluted in a similar manner with pure distilled water. Total N as $\text{NH}_3 = 7.8787$ mg. 100 of each was treated with $3'' \times 2''$ copper-zinc couple.

				Soft Water.	Hard Water.
Milligrammes of NH_3	7.8787	10.1412
In 2 days	1.3	2.5
„ 4 „	4.0	4.25
„ 6 „	7.8	10.1

It would seem from this as if the hardness of the water has little or no effect upon the time required; indeed a hard water seems to be reduced the easier of the two, but the quantity of zinc exposed is no doubt the chief factor in the duration of time, as may be seen from the following experiments:—

Water containing—

Total solids	1040.0	} Total Am by CuZn 12.5 milligrammes per litre.
Free Am	0.09	
Alb. „	0.12	
N	10.23	

Three lots of 70 c.c. were treated with CuZn couples, having the respective surfaces of (a) 4 sq. in., (b) $2\frac{1}{2}$ sq. in., (c) $1\frac{1}{2}$ sq. in.

		(a)		(b)		(c)
In 24 hours (5 c.c.)	..	.032	..	.0272	..	.020
„ 48 „	..	.0625	..	.0625	..	.035
„ 72 „	..	—	..	—	..	.045

$.0625 \times 200 = 12.5$, the total amount present.

Here we see in a very hard water complete reduction took place in two days with only $2\frac{1}{2}$ sq. in. of zinc. The sample having 4 sq. in. was probably finished earlier.

From these and other results, I concluded it was better to err by using too much zinc than too little, and that eight sq. in. should be invariably employed. By so doing the time required for reduction is seldom prolonged beyond the twenty-four hours. Of course I am speaking of my own experience only. It may happen that others may obtain different results. The waters in my district are generally hard, some very much so, due to the proximity of the lias. They are also highly charged with chlorine from salt deposits in the soil. (We have an artesian well just beyond the town, which is of no use to anybody on account of the salinity of the water.) This may probably tend towards rapidity, whereas, according to Mr. Williams' original paper on this subject (ANALYST, Vol. VI., p. 36), the presence of salts with an alkaline re-action is found to retard the speed of the reduction.