

SUPPLEMENTARY NOTES ON "A NEW AND RAPID METHOD FOR THE DETERMINATION OF NITROGEN IN ORGANIC BODIES."

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IN a communication read before the May meeting of the Society of Public Analysts (*see THE ANALYST*, June, 1892, page 109), I pointed out that the nitrogen of certain organic bodies, of which a list was given, could be rapidly converted into ammonia by treatment with manganese dioxide in presence of strong sulphuric acid. I was not present at the meeting, and as the direction of the discussion was distinctly adverse to the method I proposed I feel that it is due to the members who were present on that occasion that I should take the earliest opportunity of showing them that the method is far from being an unimportant one.

A good deal was said about the danger of the ammonia formed being acted upon by the manganese dioxide. Now it will be found on reference to the paper, that in my experiments the relation of manganese dioxide to nitrogen present ranged from 141 to 1 to 66 to 1. Also that the exposure of the substance to the action of the dioxide was not a "time" exposure—that is, the reaction was allowed to proceed until green coloration of the mass ensued without respect to time. And yet the results agreed most perfectly. I

imagined that these considerations were quite sufficient in themselves to dispose of any fear on this point.

It appeared, too, that my not giving details of analyses of pure ammonium salts was considered an important omission, but this was certainly far from what I intended. I meant to show that my method would deal perfectly with *Nitrogen in organic combination*. I said so at the outset, and consistently stuck to my text. But believing that facts are of greater value than argument, I beg to quote the following experiments as further evidence that ammonia is not lost in the "rapid" process :—

Analysis of Ammonium Chloride.

0.4922 grm. taken. Nitrogen calculated, 0.1288 grm. Nitrogen found, 0.1276 grm.

Analysis of Ammonium Oxalate.

0.4934 grm. taken. Nitrogen calculated, 0.0973 grm. Nitrogen found, .0965 grm.

It was stated during the discussion that I had admitted having entirely failed with ferrocyanide. What I said was that "attempts had been made—but so far without success." I knew when I wrote the paper where the want of success lay, and I have since corrected the error, as will, I think, be seen by the following :—

Analysis of Potassium Ferrocyanide.

0.5 grm. taken. Nitrogen calculated, 0.0994 grm. Nitrogen found, 0.0996 grm.

0.5 " " " 0.0994 " " " 0.0996 "

0.5 " " " 0.0994 " " " 0.0988 "

To the statement made that the analyses of uric acid are not in close agreement I hardly think it necessary to reply. A difference of 0.19 per cent. is mild as compared with what one sometimes sees in the data from which the formula of a substance is calculated; and, speaking as an analyst of long experience, I should be glad if I could always get within two-tenths of a per cent. of "the constituent sought."

These, then, were the points in the discussion which seemed to necessitate some further notice at my hands, but I should like to add that analysts have few "universal" processes, and I do not ask the members of this Society to look upon the method of procedure which I have had the honour of laying before them as universally applicable. What I do claim for it is, that with many substances the time needed for oxidation is shortened to 3 or 4 minutes; that it does away with special flasks, ordinary beakers may be used, and this greatly facilitates the work; that it dispenses with the use of mercury and consequently of potassium sulphide; that there is no need for zinc in the distillation and that fracture of the distilling flask is impossible; and, finally, that when thoroughly understood, it is capable of very wide application, yielding results which are perfectly satisfactory. I am myself using the process regularly with a degree of ease, accuracy and speed that I never expected to attain in the determination of nitrogen.

This terminated the Society's proceedings.

The Analysis of Substitutes for Coffee. Moscheles and R. Stelzer. (*Chem. Zeit.* 1892, xvi. 281, 282.)—The property which most readily distinguishes coffee substitutes from genuine coffee is usually their freedom from caffein. Some such substances have been found to contain the bitter principle of the lupin as a substitute for caffein—a most reprehensible addition. Quite recently a coffee surrogate was examined by the authors which contained powdered kola nut, which is known to contain caffein. In distinguishing analytically between coffee and its substitutes the determination of the percentage of fat and of total extractive matter is of value. The amount of fat in coffee varies between 7 and 16 per cent., while in the factitious article it is considerably lower, namely, from 0 to 8%. The total extract from coffee is about 20-30%, while that of coffee substitutes usually varies from 50-75%. The process of analysis is hampered by the difficulty of obtaining a clear solution of the total soluble matter in the coffee, and at the same time making certain of thorough extraction. The filtration of such a solution is difficult, and it commonly becomes turbid on cooling, from the precipitation of gum, dextrin, and similar bodies. The authors have, in consequence, abandoned the attempt to obtain perfect extraction, the more readily because it does not represent what takes place in the actual use of coffee. Their practice is to powder finely 25-30 grms. of the substance and digest it for half-an-hour on the water-bath with 500 c.c. of water. The solution is made up to one litre, allowed to cool and a portion drawn off and evaporated to dryness, with the addition of a weighed quantity of ignited sand, to constant weight. This represents the extract obtained under ordinary domestic conditions. The following results were obtained with some modern coffee surrogates:—

CHICORY MALT COFFEE FROM R. BAER, BERLIN.								
Extract	36.00%
Moisture	2.65
Woody fibre	12.93
Natural ash	2.11
Sand	0.05
Soluble proteids	0.25
Gum and dextrin	24.14
Sugar...	4.90
Starch, etc.	42.13
Fat	1.84
Caffein	—
Linde.								
				Linde Bros.' Coffee.		Linde Bros.' Coffee Essence.		Feine's Malt Coffee.
Extract	68.14	...	72.03	60.33
Soluble proteids	4.61	...	4.56	7.56
Sugar and dextrin	59.38	...	59.53	59.37
Other extractive substances	35.81	...	35.81	33.07
Moisture...	4.63	...	3.23	2.13
Ash	5.03	...	2.35	1.87

COFFEE SUBSTITUTE OF UNKNOWN ORIGIN.

Extract	46.52%
Soluble proteids	13.94
Nitrogenous extractive material	5.18
Non-nitrogenous extractive material	18.88
Sugar	12.00
Soluble salts	2.32
Moisture	8.01
Fat	4.27
Woody fibre	22.04
Natural ash	0.74
Sand	0.48
Caffein	0.31

In all cases the proteid and extractive substances given above are those in the "extract" which was obtained by the method already described, no attempt at complete extraction being made.

B. B.

The Determination of Crude Fibre. S. Gabiel. (*Zeits. Physiolog. Chem.*, 1892, xvi., 370, through *Chem. Zeit.*)—The author has examined Hönig's method for the determination of crude fibre and starch. The method in question depends upon the fact that albumen and starch become soluble in water, after heating with glycerine to 210° C, while cellulose is not attacked. As the process was employed by the author solely for the determination of crude fibre, the whole of the operations for the separation of the starch could be omitted. In place of the sulphuric acid bath, used by Hönig, the author found that a naked flame could be more conveniently employed, as regulation of the temperature was thereby rendered easier. Certain modifications were necessary, on account of the nitrogenous and non-nitrogenous substances, other than cellulose, being unattacked by glycerine alone. The requisite additional activity of the attacking reagent can be obtained by the use of a caustic alkali, and the method thus modified, is carried out as follows:—2 grms. of the substance are heated, in a 250 c.c. flask, on a piece of wire netting, over a naked flame, with 60 c.c. of a solution of caustic alkali in glycerine, containing 33 grms. of caustic potash per litre. A vigorous reaction sets in usually at about 130° C, at which point precaution is necessary to moderate the foaming that takes place. At a temperature of 160° C, the reaction is for the most part finished, after which the temperature is gradually raised to 180° C. The product is then emptied into a dish containing 200 c.c. of boiling water, well stirred, allowed to settle thoroughly, and the supernatant liquor drawn off with a syphon, having a piece of linen tied over the end. The residue is then boiled up again with 200 c.c. of water, and a third time with the same quantity of water, to which has been added 5 c.c. of 25 per cent., hydrochloric acid. The unattacked crude fibre is washed with alcohol and ether, as in the Wendeer method. The extremely small quantity of nitrogenous substances left in the crude fibre appears to be, in most cases, negligible.

B. B.

A Simple Method for the Detection of Frozen Meat. Maljean. (*J. Pharm. Chim.*, 1892, xxv. 348, through *Chem. Zeit.*)—The process adopted by the author for distinguishing between fresh meat and that which has been preserved in the frozen state, consists in expressing a little blood or meat juice from the sample, and examining it under the microscope. The whole operation must be performed quickly, in order to prevent any drying up of the liquid under examination. When the juice of fresh flesh is thus examined, it is seen to contain numerous red corpuscles, which are normal in colour, and float in a clear serum. In the case of blood from frozen flesh, the corpuscles have dissolved in the serum under the influence of the low temperature, and not a single normal red corpuscle can be seen. The hæmoglobin escapes into the serum, and appears as irregular, yellow-brown crystals. These may be frequently seen by the naked eye, but, in every case, can be readily detected under the microscope. B. B.

The Determination of Glycerine in Wine. M. T. Lecco. (*Chem. Zeit.*, 1892, xvi., 504.)—The usual method of determining glycerine in wine is that officially recognised by the Berlin Committee of 1884, although it is far from ideal. The residue which is obtained by evaporating the wine together with quartz sand and milk of lime nearly to dryness, is difficult to remove from the dish in which the evaporation has been performed, and a certain quantity of glycerine is apt to be left in the residue after extraction. The following are the modifications proposed by the author:—10 c.c. of the wine are well mixed with 0.1 of a grm. of powdered calcium hydrate, 10 grms. of quartz sand added, and the whole evaporated almost to dryness on the water bath. The residue is extracted four or five times with hot absolute alcohol, and the extract, amounting to 40—50 c.c., is filtered into a flask holding about 100 c.c., then evaporated on the water bath the syrupy residue dissolved in 5 c.c. of alcohol, 7.5 c.c. of ether added, the flask well corked, allowed to stand some hours, and the clear solution poured into a weighed flask (previously filtering if necessary), the alcoholic liquid evaporated off, and the residue dried for one hour in the water oven and weighed. This method, when tried on seven samples of Servian wine, containing from 0.7 to 1.0 per cent. of glycerine, gave results ranging from 0.1 to 0.36 per cent. higher than the old method; while, at the same time, closely concordant results were obtained by repetitions of the new method, and also when it was carried out on a scale ten times as great as that prescribed above. In order to ascertain whether the compound formed of lime and glycerine by evaporation to complete dryness resisted the solvent action of the alcohol, further experiments were made in which this condition obtained, with the result that the percentage of glycerine found was not diminished, but slightly increased. Should this observation be confirmed, the need for special precaution in the evaporation will be obviated. The author also states that he has obtained good results by evaporating an aliquot portion of the alcoholic extract, by which means previous filtration and washing necessary to the original process are avoided. He has yet to prove the purity of the glycerine thus isolated. B. B.