

NOTES ON THE ESTIMATION OF CAFFEIN.

BY W. A. PUCKNER.

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SOME time ago Gomberg published a method for the estimation of caffein, by means of Wagner's reagent,¹ wherein appear certain statements from which is to be inferred the superiority of this method over such where the caffein is shaken out of an aqueous solution by means of chloroform, and which, if true, would show that most methods now in use, give low results since but an imperfect separation of caffein is attained. Thus Spencer² is said to have demonstrated the difficulty with which the alkaloid is abstracted from watery solutions, he directing that at *least* seven portions of chloroform be used for this purpose, but offering no proof of the necessity for this departure from the usual direction of shaking out the liquid with three or four portions of the solvent. Spencer is at variance with Allen,³ who investigated this matter and found that from a solution, slightly acidulated with sulphuric acid, one treatment with chloroform removed seventy to eighty-five per cent. of the amount present, while four usually effected complete extraction, especially if toward the end the solution is rendered faintly alkaline.

This agrees well with the results of my own experiments, where anhydrous caffein, in quantities from one-tenth to four-tenths gram, dissolved in fifty cc. one per cent. sulphuric acid, was shaken successively with twenty-five, ten and ten cc. chloroform, the united chloroform solution evaporated at a gentle heat and the residue dried over sulphuric acid to constant weight. In each case the solution was shaken with a further quantity of ten cc. chloroform and the weight of the caffein so extracted ascertained as before.

Caffein taken. Gram.	Residue from first, second and third extraction. Gram.	Residue from fourth extraction. Gram.	Total per cent. recovered.
0.1285	0.1277	0.0004	99.69
0.1852	0.1820	0.0026	99.67
0.1988	0.1980	0.0002	99.69
0.2011	0.1977	0.0025	99.55
0.2559	0.2552	0.0005	99.92
0.4416	0.4355	0.0043	99.58

¹ This Journal, 18, 331.

² J. Anal. Chem., 4, 390.

³ Com. Org. Anal., 3, Part II, 485.

1.0137 gram caffein, rendered anhydrous by keeping in a desiccator over sulphuric acid until its weight remained constant, was dissolved in sixty cc. ten per cent. sulphuric acid and shaken successively with nine portions of chloroform, twenty-five cc. each; the chloroform solutions evaporated at a gentle heat and the residue dried over sulphuric acid to constant weight.

1st portion of twenty-five cc. yielded a residue of	0.5525	gram.
2nd " " " " " " " " " "	0.2514	" "
3rd " " " " " " " " " "	0.1155	" "
4th " " " " " " " " " "	0.0535	" "
5th " " " " " " " " " "	0.0237	" "
6th " " " " " " " " " "	0.0114	" "
7th " " " " " " " " " "	0.0058	" "
8th " " " " " " " " " "	0.0029	" "
9th " " " " " " " " " "	0.0015	" "
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	1.0182 ¹	" "

In the second experiment 1.0001 gram anhydrous caffein in sixty cc. ten per cent. sulphuric acid, extracted as before, with chloroform in proportions of twenty-five cc. each :

1st, 2d and 3rd portions gave a total residue of	0.9086	gram.
4th, 5th and 6th " " " " " " " " " "	0.0854	" "
7th, 8th and 9th " " " " " " " " " "	0.0134	" "
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	1.0074 ¹	" "

The sulphuric acid used in Gomberg's experiments was designated as "(1:10)" by which it is presumed an acid containing ten per cent. by weight of sulphuric acid was meant; since, however, it was possible that sulphuric acid 1:10 *by volume* was the strength of the acid used, a determination was made with an acid with such concentration, *i. e.*, ten cc. concentrated sulphuric acid mixed with water enough to make when cold, 100 cc. In sixty cc. of this were dissolved 0.9790 gram caffein and extracted with chloroform in portions of twenty-five cc. each as before.

1st, 2nd and 3rd portion yielded a total residue of	0.6484	gram.
4th, 5th and 6th " " " " " " " " " "	0.2222	" "
7th, 8th and 9th " " " " " " " " " "	0.0756	" "
10th, 11th, 12th, 13th, 14th, 15th and 16th " " " " " " " " " "	0.0379	" "
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	0.9841 ¹	" "

¹ No explanation is offered to account for the plus error in the above. Contamination with sulphuric acid was suspected, but disproved.

As was to be expected, this confirms in a general way, the statement relative the difficulty with which caffenin is shaken out of solutions containing a large proportion of sulphuric acid; in no way, however, does it agree with the data given by Gomberg, who by ten successive treatments with chloroform removed only 34.85 per cent., while my figures show that when a ten per cent. sulphuric acid was used, with but three extractions, fully ninety per cent. was recovered, and even with a still stronger acid (1 + 9 by volume), three portions of chloroform removed about sixty-five per cent.

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CONTRIBUTION TO THE KNOWLEDGE OF THE RUTHENOCYANIDES.

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POTASSIUM ruthenocyanide was described by Claus, in 1854, in his "Beiträge zur Chemie der Platinmetalle." The salt was formed by fusing ammonium rutheninitrosochloride¹ (tetrachloride of Claus) with potassium cyanide. The attempt was also made to form it by fusing potassium ferrocyanide with ruthenium, but it was found impossible to separate the ferrocyanide and ruthenocyanide. It is probable that some of Claus' experiments were carried out with a ruthenocyanide contaminated with ferrocyanide, from the fact that he describes copper ruthenocyanide as brown, whereas, when free from the ferrocyanide, it is pale green. Potassium ruthenocyanide in reactions and crystallization resembles very closely the ferrocyanide, except that when pure it is white. Its crystallography as well as that of the isomorphous ferrocyanide and osmocyanaide are described by A. Dufet.²

Preparation of potassium ruthenocyanide for the purpose of carrying out experiments upon it not yet completed, gave occasion to the work recorded in this paper.

In the Claus method of preparation, a large proportion of the ammonium rutheninitrosochloride is decomposed with separation of metallic ruthenium, and while a part of the ruthenocya-

¹ Joly : *Compt. rend.*, 108, 854, 1889; Howe : *J. Am. Chem. Soc.*, 16, 358, 1894.

² *Compt. rend.*, (1895), 120, 377.