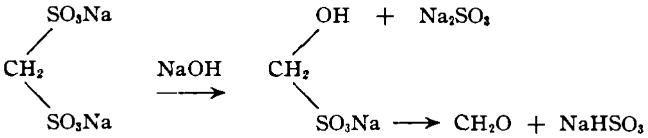
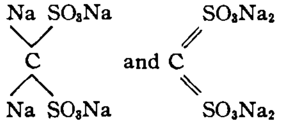


However the alkaline solution of methionic acid gave no test for sulfite. The difficulty in obtaining the points on the curve at the second break due to the failure of the hydrogen electrode to come to equilibrium rapidly is evidence in favor of some decomposition.

It has also been suggested that substitution or enolization may occur in strongly alkaline solution to give compounds of the types:



Bauer and Jenkins (1) have shown evidence for the presence of two sodiums on the carbon atom at one time by their work with diphenyl methionate, which they showed could be converted into the disubstituted derivative, $RR'C(SO_3\varnothing)_2$ in one step.

CONCLUSION.

It has been proved that methionic acid behaves as a strong dibasic acid, in the manner of sulfuric acid. It has also been shown that the second break in the titration curve is due either to decomposition or to molecular rearrangement in strongly alkaline solution.

REFERENCE.

(1) Bauer, J. C., and Jenkins, G. L., Jour. A. Ph. A., 26, 490 (1937).

A METHOD FOR EXTRACTING ALKALOIDS IN TOXICOLOGICAL ANALYSIS.*

CHARLES O. WILSON[1] AND L. W. RISING.[2]

One of the first difficulties confronting a toxicologist in his work is the efficient separation of the suspected poison from the viscera containing it. Many methods have been proposed for performing this function, particularly where alkaloids are concerned. None are without fault. Some are too time-consuming, some are very expensive, some lose significant quantities of poison and others fail to eliminate comparatively large amounts of contaminating organic material.

The importance of such weaknesses, particularly in the extraction of pure alkaloids in forensic toxicology is not to be denied, and further, the value of any new procedure designed to eliminate the more conspicuous defects, is obvious. It was in the hope of developing such a strengthened procedure that the investigation described in this paper was instituted.

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A study of the literature reveals that even up to the present time the most widely accepted methods for the extraction of alkaloidal poisons from animal tissue are based fundamentally on the precipitation of protein contaminants with ethyl alcohol. It was not until the beginning of the 20th century that toxicologists began to publish significant reports on other precipitants for this purpose. J. Greenwold (1) (1915) suggested trichloracetic acid. Gauss (2) in 1921 and Hiller and Van Slyke (3) in 1922 also found the acid practical under certain conditions. These papers indicated the feasibility of an extraction procedure which would combine the protein precipitating powers of both ethyl alcohol and trichloracetic acid. The experimental work here described substantiates the reasoning that a combination of ethyl alcohol and trichloracetic acid is an effective protein precipitant. By regulating the concentrations of each and employing them in proper order, a quick and inexpensive procedure which gives very satisfactory results was made possible.

Procedure: Mince a 50 Gm. sample in a meat grinder, add twice its weight of 2 per cent tartaric acid and warm to 70° C. Allow it to stand until the tissue particles settle. Filter the supernatant liquid and wash thoroughly with warm tartaric acid water in small portions. Place the filtrate in ice until thoroughly chilled at which time add sufficient trichloracetic acid solution to yield a final acid concentration of 2.5 per cent. Filter into an evaporating dish and thoroughly wash the residue with a 2.5 per cent solution of trichloracetic acid. Make the filtrate alkaline with sodium bicarbonate and evaporate to dryness at 60° C. Add 50 cc. of absolute alcohol to the residue and acidify with sulfuric acid. Heat for a short time on a steam-bath. Filter, washing the residue with acidulated alcohol and evaporate to dryness at 60° C. Add about 15 cc. of a 1 per cent sulfuric acid solution to the residue and filter into a 150 cc. separatory funnel. Wash carefully. Make three extractions of the acid liquid, using ether in one 10-cc. and two 5-cc. portions. The ether removes interfering substances which seem to be present in increasing amounts as the sample ages. The loss of a slight amount of alkaloid is unavoidable. Sulfuric acid appears to minimize this loss more than hydrochloric or nitric acids. Make the solution alkaline and shake out with the appropriate organic solvent. Table I lists the mean recoveries for the various poisons using this procedure. The organic solvents found best for extracting the alkaloids investigated are as follows:

Morphine Sulfate —Chloroform (9 parts), Alcohol (1 part) (According to A. O. A. C.)
Codeine Phosphate —Chloroform (According to A. O. A. C.)
Narcotine Sulfate —Chloroform (2 parts), Benzene (1 part), Alcohol (1 part)
Pilocarpine Nitrate —Chloroform (According to A. O. A. C.)
Sparteine Sulfate —Chloroform (4 parts), Ether (1 part)
Veratrine Hydrochloride—Ether (4 parts), Alcohol (1 part).

TABLE I.

Alkaloidal Salt.	Amount.	Sheep Stomach.	% of Recovery.
Morphine Sulfate	100.0 Mg.	50.0 Gm.	96.4
Codeine Phosphate	100.0 Mg.	50.0 Gm.	94.1
Narcotine Sulfate	100.0 Mg.	50.9 Gm.	95.0
Pilocarpine Nitrate	100.0 Mg.	50.0 Gm.	94.2
Sparteine Sulfate	100.0 Mg.	50.0 Gm.	95.1
Veratrine Hydrochloride	100.0 Mg.	50.0 Gm.	96.2

The silicotungstic acid method of North and Beal (4) was used for the quantitative determination of codeine, narcotine, pilocarpine and sparteine. In this method the organic solvent containing the alkaloid is volatilized, the alkaloidal residue dissolved in acid water, then precipitated with 5 per cent silicotungstic acid. The precipitate is collected on ashless filter paper and ignited. The amount of alkaloid in the sample can be calculated from the weight of the oxides produced.

The phosphotungstic acid method of A. Heiduschka and L. Wolf (5) gave more uniform results in the determination of morphine and veratrine.

The extraction method was also tested to determine the smallest amount of morphine sulfate which could be extracted from a definite quantity of sheep stomach. The results are expressed in Table II and show that qualitative tests are possible when the ratio of morphine sulfate to tissue is as small as 1:500,000.

TABLE *II.*

Morph. Sulf.	Sheep Stomach.	Proportion.	Lefort's.	Marquis.	Results.
0.0 mg.	250.0 Gm.	00:00	–	–	–
10.0 mg.	250.0 Gm.	1:25,000	+	+	+
10.0 mg.	250.0 Gm.	1:25,000	+	+	+
10.0 mg.	250.0 Gm.	1:25,000	+	+	+
2.5 mg.	250.0 Gm.	1:100,000	+	+	+
2.5 mg.	250.0 Gm.	1:100,000	+	+	+
2.5 mg.	250.0 Gm.	1:100,000	+	+	+
1.0 mg.	500.0 Gm.	1:500,000	+	+	+
1.0 mg.	500.0 Gm.	1:500,000	+	+	+
1.0 mg.	500.0 Gm.	1:500,000	+	+	+
.5 mg.	500.0 Gm.	1:1,000,000	–	+	–
.5 mg.	500.0 Gm.	1:1,000,000	–	–	–

SUMMARY.

1. A method was developed for extraction of morphine sulfate, codeine phosphate, narcotine sulfate, pilocarpine nitrate, sparteine sulfate and veratrine hydrochloride from animal tissue.
2. The delicacy of the procedure for qualitative extraction in the case of morphine sulfate was examined.

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(2) Gauss, *Jour. Lab. and Clinical Med.*, 6, 699 (1921).
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(5) Heiduschka and Wolf, *Scheitz Apoth. Ztg.*, 58, 213 (1920); *Chem. Abstracts*, 14, 3041 (1920).

ON THE REDUCTION OF THE ALKALINITY OF HYPOCHLORITE SOLUTIONS WITH SODIUM BICARBONATE.*

BY ARTHUR OSOL[1] AND JOHN ROGER COX.[1]

In the commercial preparation of solution of sodium hypochlorite an excess of sodium hydroxide or sodium carbonate usually remains in the product. For many purposes such alkalinity is not disadvantageous but for application to wounds dilutions of this solution should be nearly neutral in reaction. To attain to this end the U. S. P. XI directs that in the preparation of diluted solution of sodium hypochlorite from the stronger solution, a sodium bicarbonate solution shall be added until no red color is produced with powdered phenolphthalein.

The mechanism of this neutralization of caustic alkalinity by the addition of sodium bicarbonate has been reported as consisting of the repression of ionization of sodium hydroxide in the solution by the added sodium ion, the law of mass action

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