Substitution of Gasoline for Ether in Morphine Determination in Opium Dross.

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Introduction

For almost 15 years the Department of Science (formerly known as the Government Laboratory) has taken over the task of determining the morphine content of opium and opium dross by means of quantitative analysis. The prevailing analytical method was brought over from the Straits Settlement of Malay. By opium is here meant prepared opium stuff which is ready for consumption. Opium dross is the remnant of smoked opium, the greater part of which is ash mixed with a small quantity of unburnt opium.

The method employed at present is quite satisfactory in so far as its execution and results are concerned. An enormous number of samples both of opium and opium dross pass through the Opium Section of the Department of Science annually. The highest mark attained was in B. E. 2479 when the total opium dross samples alone numbered 19,380.

Malay (F. M. S.) Method.

The method employed is as follows. Weigh out 5 grams of opium dross or chandu in a beaker and disintegrate, using heat if necessary, with about 50 cc. of water. Transfer into a graduated cylinder and dilute to 102 cc. (2 cc. are allowed for volume of tannic acid precipitate). Shake and filter into a 100 cc. graduated cylinder.

Take 80 cc. of the clear filtrate which is equivalent to 4 grams of the sample, warm and precipitate the excess lead acetate with hydrogen sulphide gas. Filter and wash the precipitate once or twice with hydrogen sulphide water. Evaporate the filtrate to a few

cc. Transfer into a 50 cc. conical flask using as little water as possible.

Add 3 cc. of alcohol, 2 cc. of strong ammonia and 25 cc. of ether. Stopper the flask securely with an India rubber stopper, shake for an hour and set aside over night. Filter by pouring the ethereal layer through a small filter, wash the aqueous solution and crystals 3 times with ether using 8 cc. each time and allow the ether to evaporate from the filter paper. Transfer the aqueous solution and crystals to the same filter paper and wash with a saturated solution of morphine.

Dry the precipitated crystals in a hot air oven to remove ammonia. Place the filter paper with crystals in a beaker and add to it 25 cc. of standard sulphuric acid (i. e. 1 cc. N/10 H_2SO_4 = exactly 0.0285 grams of anhydr. morphine). Leave the solution standing for at least 2 hours and titrate it with standard sodium hydroxide solution, using methyl red as indicator.

Purpose of Modifications

It is internationally conceded that no one method of analysing opium should be accepted as applicable or suitable for all countries as even the method of mixing opium varies in each country. The analytical method of the F. M. S. differs from ours when both were recently compared. Scientific methods change with the time and place, so that scientists are always working to find out the most suitable method to solve a problem. The Opium Section, in accordance with this tradition, is ever working out new procedures which give better results and at the same time are both convenient and economical.

The Malay method of determining morphine in opium and opium dross, though very satisfactory, involves the use of some expensive chemicals. After due deliberation it seemed necessary to choose one of the following alternatives.

a. Adopting an entirely different method.

b. Using the same method but substituting some chemicals for others.

Experimental.

The first alternative has been tried with no success, as no method could be discovered that would be suitable for prevailing conditions. So the latter alternative had to be taken into consideration. A close examination of the chemicals involved revealed the fact that some could even be omitted altogether e. g. lead acetate and hydrogen sulphide, and gasoline could be substituted for ether. In a preliminary trial the acetate and sulphide were omitted from the process and the results were favourable.

Table I.

Comparison of Results of the Malay and the Modified methods.

Lab. No.	Malay method % morphine	Modified method, not using lead acetate and hydrogen sulphide % morphine	Differences %
83/923	5.8	5.8	—
924	6.6	6.5	− 0.1
925	5.5	5.5	—
926	6.7	6.7	—
927	7.1	7.2	+ 0.1
928	6.5	6.5	—
929	5.7	5.8	+ 0.1
930	6.3	6.3	—
931	5.6	5.8	+ 0.2
932	6.5	6.5	—
933	6.0	6.1	+ 0.1
934	7.1	7.1	—
958	8.7	8.7	—
959	8.0	8.1	+ 0.1
960	6.4	6.3	− 0.1
961	9.1	9.2	+ 0.1
962	8.0	8.0	—
963	7.3	7.3	—
964	2.4	2.5	+ 0.1

The results obtained, when lead acetate and hydrogen sulphide were omitted, compared quite favourably with those of the old routine method. It will be observed that the two processes yield somewhat different results. But this fact cannot be attributed to any fault inherent in the new process. Even with an identical sample and an identical process, successive results may be different. This is because for each procedure there are unavoidable varieties in the operation so that it is impossible that one result should be identical with another. The reason why lead acetate is not used with opium dross here are that the dross is composed mostly of ashes and only a little amount of opium. Hence the use of lead acetate is unnecessary.

After thorough examination of the whole process of opium dross analysis, it became evident that most probably a change of solvent would also give good results.

Ether is used for the collection of morphine precipitate which separates from opium dross, as the precipitate is practically insoluble in the said liquid (1 : 5000 appr.). When the experiment was conducted to ascertain the solubility of morphine in gasoline it appeared that morphine was not at all soluble. This result lead to the experimentation with an aim to substitute gasoline for ether, using the Malay process with the omission of lead acetate and hydrogen sulphide.

SPECIFICATIONS OF GASOLINE USED IN THE METHOD OF ANALYSIS

Sp. gr. of gasoline 64° Be′ (0.7238) $\frac{60°}{60}$F.

Distillation test indicates the presence of the following hydrocarbon fractions.

Initial drop 36.1°C.

TABLE II.

Fractions of Gasoline used.

At Temperature (°C)	Total Distillate % by volume
68.0	10.0
80.0	20.0
88.5	30.0
96.0	40.0
102.0	50.0
108.5	60.0
116.0	70.0
126.5	80.0
140.5	90.0

Vapor pressure	=	6.8 lbs. per sq. inch.
End point	=	160.5°C.
Total distillate	=	96.5 %
Loss	=	2.7 %
Residue	=	0.8 %

TABLE III.

Determination of Morphine Contents in Opium Dross.

Lab. No.	Modified method using gasoline % morphine	Modified method using ether % morphine	Differences %
83/488	7.7	7.8	+ 0.1
489	6.6	6.6	—
508	1.1	1.2	+ 0.1
512	4.7	5.0	+ 0.3
513	6.2	6.3	+ 0.1
514	7.0	7.2	+ 0.2
515	6.5	6.7	+ 0.2
516	5.9	6.1	+ 0.2
83/517	6.5	6.7	+ 0.2
518	6.2	6.3	+ 0.1
616	5.8	5.8	—
617	8.0	7.9	− 0.1
618	8.0	7.8	− 0.2
619	6.6	6.3	− 0.3
620	7.4	7.4	—
621	6.9	6.8	− 0.1
622	5.6	5.6	—
623	5.2	5.1	− 0.1
624	6.3	6.2	− 0.1
625	6.9	6.9	—
626	8.2	8.1	− 0.1

From the above data it is evident that the results obtained through the use of either solvent, are very close, the difference in favor of gasoline is up to 0.3%. Careful comparison of results shows that in most cases the quantity of morphine is found to be greater, when using gasoline instead of ether. The experiment was repeated using redistilled gasoline in order to ascertain whether commercial gasoline may contain impurities which would affect the result.

TABLE IV.

Comparison of Results using Redistilled and Common Gasoline.

Lab. No.	Modified method using redistilled gasoline % morphine	Modified method using commercial gasoline % morphine	Difference %
83/764	6.4	6.6	+ 0.2
765	7.2	7.5	+ 0.3
766	5.6	5.8	+ 0.2
767	7.4	7.5	+ 0.1
768	6.3	6.5	+ 0.2
769	6.3	6.6	+ 0.3
770	5.9	5.7	− 0.2
771	5.1	5.1	—
772	8.0	8.3	+ 0.3
773	6.3	6.2	− 0.1
821	6.8	6.6	− 0.2
828	6.2	6.4	+ 0.2
829	8.5	8.8	+ 0.3
830	7.4	7.7	+ 0.3
831	5.5	5.6	+ 0.1
832	6.9	7.2	+ 0.3

The use of either commercial or redistilled gasoline makes no difference in the results. Both commercial and redistilled gasoline yield up to 0.3% of morphine in excess over those obtained with ether.

Discussion.

The use of gasoline instead of ether is not only practical in opium dross analysis but may be suitable for the extraction of other alkaloids which are now extracted by ether. Long experience has shown that gasoline and ether have the following properties.

Use of ether	Use of gasoline,
1. Expensive.	1. Comparatively cheap.
2. Greater loss during distillation : 3 parts out of 5 are recovered.	2. Smaller loss, more than 4 parts out of 5 recovered.
3. A number of chemicals must be used for recovery.	3. No chemical used for recovery.
4. Highly inflammable hence more dangerous.	4. Less inflammable, less dangerous.
5. Morphine precipitate not so white.	5. Morphine precipitate whiter in color, containing less impurities.

In substituting gasoline for ether in the analytical method of determining morphine in opium dross, economy is not the only consideration. A careful examination of the process reveals no marked disadvantages.

The use of ether is for collecting morphine precipitate as it is almost insoluble in ether. Since morphine is not soluble in gasoline it is therefore even a better precipitating agent for morphine.

Summary.

The advantages of the new procedure may be summarized as follows :

1. The quantitative determination of morphine in Thai opium dross may be carried out without employing lead acetate.

2. Omission of lead acetate results in saving of time and other chemicals such as sulphuric acid and iron sulphide.
3. Hydrogen sulphide fume is eliminated.
4. Gasoline may be used instead of ether in morphine determination.
5. Use of gasoline instead of ether results in a morphine precipitate, whiter in colour, as well as in greater economy.
6. The gasoline used in this process had the following specification: at 144°C. the total distillate amounted to 90% by volume.
7. Recovery of gasoline by distillation is simpler and less costly than that of ether.