hot and grayish-white when cold. At this point the operation is finished and the boat containing the molybdenum trioxide is weighed.

This method, which requires only a short time for completion, is applicable for organic and inorganic substances provided they contain no other non-combustible or non-volatile constituents.

Results.—Some of the results obtained are as follows.

Molybdic Acid. 56.67% of Molybdenum. Macro Analysis.

Sample taken, mg.	3.105	2.275	2.442	3.250
MoO_3, mg.	2.642	1.934	2.075	2.758
Molybdenum found, %	56.71	56.68	56.62	56.58

Ammonium Molybdate. 53.87% of Molybdenum. Macro Analysis.

Sample taken, mg.	4.155	5.675	3.786	2.667
MoO_3, mg.	3.339	4.576	3.045	2.144
Molybdenum found, %	53.57	53.75	53.53	53.59

Histamine Molybdate. Calcd., 48.24% of Molybdenum.

Sample taken, mg.	3.936	5.017	4.406
MoO_3, mg.	2.852	3.664	3.202
Molybdenum found, %	48.30	48.60	48.45

Summary

A rapid gravimetric micro method for the quantitative determination of molybdenum in organic compounds has been described.

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[Contribution from the Department of Physics, University of Michigan]

I. PURIFICATION OF METHYL FLUORIDE
II. QUANTITATIVE GAS ANALYSIS BY HIGH DISPERSION INFRA-RED SPECTROSCOPY

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Besides the interest in a ready method for preparing pure methyl fluoride, it is thought that this investigation will be of interest inasmuch as an application of infra-red spectroscopy is made in determining the purity of an organic compound with greater accuracy than is available through the usual chemical methods.

The best method for the preparation of methyl fluoride which a search of the literature revealed was that of E. Moles and T. Batuecas.[1] They prepared silver fluoride by recrystallization and warmed with methyl iodide, purifying the vapors by repeated warming with silver fluoride. Their test of purity consisted of bringing the methyl fluoride gas to constant density by purification. They also tried the method of heating

[1] Moles and Batuecas, *J. chim. phys.*, **17**, 537 (1919).

potassium methyl sulfate with potassium fluoride and found that by the density determination method, they obtained 95% methyl fluoride at first, and then successively less methyl fluoride with each preparation, so the method was abandoned. It was stated that in all probability the impurity was methyl ether.

This investigation began with an attempt to find a method for the elimination of the methyl ether from the methyl fluoride prepared by the latter method, since the crystallization of silver fluoride is such a time-consuming operation.

Erlenmeyer and Kriechbaumer[2] give a method of preparation of methyl ether. Methyl alcohol is heated with concentrated sulfuric acid and the gas evolved is passed into concentrated sulfuric acid, which absorbs 600 volumes of methyl ether. This sulfuric acid solution is run into an equal volume of water, when 92% of the methyl ether is recovered. It was thus thought that concentrated sulfuric acid would be a good absorbent of methyl ether.

Potassium fluoride hydrate, $KF\cdot 2H_2O$ (Baker), was heated until the water of crystallization had boiled off, leaving a white mass of anhydrous potassium fluoride, KF. This was pulverized. Potassium methyl sulfate, crystalline KCH_3SO_4 (Eastman), was pulverized and mixed with the pulverized potassium fluoride in the ratio of two parts of KF to five parts of KCH_3SO_4. The mixture was heated to 140–200°. The gas evolved was passed (1) through concentrated sulfuric acid in a spiral wash bottle with a gas path of about 65 cm., (2) through a concentrated solution of potassium hydroxide, (3) through a drying tube of soda lime and two drying tubes of calcium chloride (fused), and (4) into a condenser submerged in liquid air.

Methyl fluoride is solid at the boiling point of liquid air, so care had to be exercised to keep solid methyl fluoride from plugging the entrance tube to the condenser bulb. The middle fraction was taken from the methyl fluoride boiling out of the condenser on lifting the latter from the liquid air.

The impurities to be expected from reactions occurring in heating $KF + KCH_3SO_4$ are CO_2, H_2O, $(CH_3)_2O$, C_2H_4 and SO_2. The KOH is known to absorb CO_2 and SO_2 quantitatively, and $CaCl_2$ absorbs the H_2O.

Three samples of methyl fluoride were prepared. Sample A was prepared by removing the sulfuric acid bottle from the purification train, the gas being passed into the spectroscopic absorption cell without condensing with liquid air. Sample B was made without the sulfuric acid bottle also, but it was fractionated from liquid air. Sample C was prepared pure as above described.

The spectra of these three samples were measured on the high dispersion spectrometer in this Laboratory. A fairly large range of wave length of the radiation from a Nernst glower was selected by a fore-prism spectrometer. This radiation was passed through the gas cell and allowed to fall on the entrance slit of the grating spectrometer. A Michigan echelette grating ruled on a solder surface with 1440 lines per inch was used to further disperse the beam. The exit slit selected a narrow range of wave length of radiation which fell on a junction of a Pfund thermopile. The current from the thermopile was amplified by means of a Moll-Burger thermo-relay. The current from this relay was measured by means of a high sensitivity Leeds and Northrup galvanometer.

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[2] Erlenmeyer and Kriechbaumer, *Ber.*, 7, 699 (1875).

The gas cell was built of brass and was provided with rock salt windows. It was sealed so that the rise of pressure, after evacuation, was about 0.1 mm. in the course of two days. A pump, a manometer and a McLeod gage were used for controlling and measuring the pressure of gas used in each spectroscopic measurement.

A more detailed description of the apparatus and of the method of observation is being published concurrently with this.[3]

A preliminary inspection of the spectra when plotted showed that samples A and B contained methyl ether but that sample C contained practically none of the ether. The spectra of none of the samples showed any similarity to the spectrum of the band in this region for ethylene, so it was definitely concluded at the outset that none of the latter gas was present.

In a previous communication[4] the variation of infra-red absorption in liquids with cell thickness was studied and it was found experimentally that for small cell thicknesses the absorption is approximately proportional to the thickness. Since the fine structure of the spectrum of the methyl ether is not resolved with the slit width used, the absorption of the gas will vary with gas concentration in the cell in the same manner that it does with cell thickness in the case of liquids, and the percentage absorption will be porportional to the gas concentration for small percentage absorptions, to within the accuracy of these measurements. The validity of this assumption was checked by measuring the spectrum of pure methyl ether at 2 cm. and 4 cm. pressure, and the respective absorptions were found to differ by a factor of 2, to within the experimental error stated later.

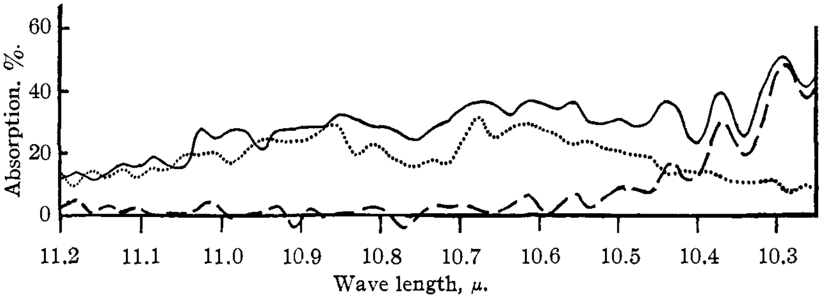

Fig. 1.

Fig. 1 shows the absorption spectra in the region 10.3 μ to 11.2 μ of these samples. No essential difference was found in the spectra of samples A and B and these, with the absorption cell filled at 73.6 cm. pressure, are shown as the full line. The spectrum of sample C at 73.7 cm. pressure

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[3] Willard H. Bennett and Charles F. Meyer, "The Infra-red Absorption Spectra of the Methyl Halides," *Phys. Rev.*, 32, 888 (1928).

[4] Willard H. Bennett and Farrington Daniels, THIS JOURNAL, 49, 50 (1927).

is shown as the broken line and the spectrum of methyl ether at 2.0 cm. pressure is shown as the dotted line. Fig. 2 shows that part of the 10-μ band for ethylene at a low pressure which lies in this region.[5] In Fig. 3, the full line represents the observed absorption percentages for the purified methyl fluoride at 73.7 cm. pressure. The dotted line represents the absorption of the empty cell.

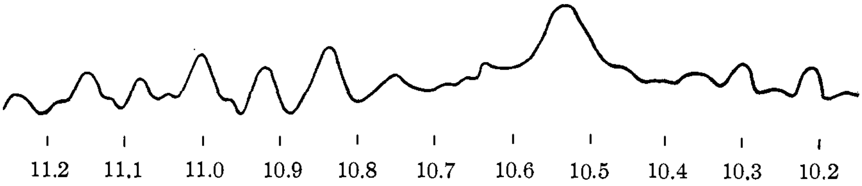

Fig. 2.

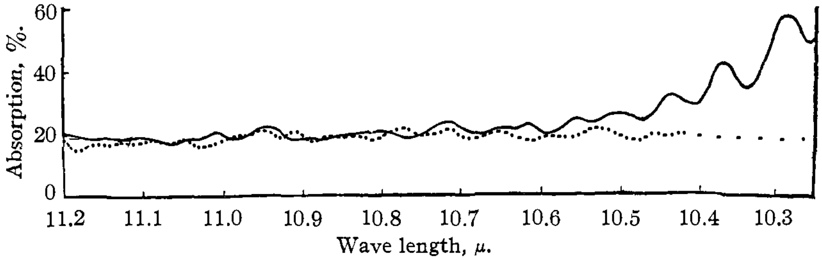

Fig. 3.

From data compiled in Table I, the percentages of methyl ether present in samples A and B were determined. The range of wave length from 10.8 μ to 11.2 μ was deemed the most representative. Readings were taken at 2′ intervals of circle setting as given in Col. 1. Cols. 2, 3 and 4 give the percentages of absorption of samples A and B and methyl ether, respectively. Cols. 5 and 6 give the ratios of the absorption of methyl ether to the absorptions of samples A and B, respectively. By the method of least squares, the value of the ratios for samples A and B are 118 ± 4% and 123 ± 4%, respectively. Since the methyl ether spectrum was measured with the gas at 2.0 cm. pressure, while the spectra of samples A and B were both taken at 73.6 cm. pressure, the molar concentrations of methyl ether in samples A and B are

$$\frac{2.0}{73.6}(1.18 \pm 0.04) \text{ and } \frac{2.0}{73.6}(1.23 \pm 0.04)$$

or 3.08 ± 0.10% and 3.21 ± 0.10%, respectively. Hence fractionation from liquid air has not removed methyl ether to within the probable experimental error, which is 0.10%.

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[5] A. Levin and C. F. Meyer, *J. Opt. Soc. Am.*, **16**, 137 (1928).

TABLE I

EXPERIMENTAL DATA

1	2	3	4	5	6
38 30	12.0	13.5	13.5	89	100
28	13.5	14.0	9.5	142	147
26	12.5	16.5	14.0	89	118
24	13.5	16.5	12.0	112	137
22	16.5	16.0	14.5	114	110
20	15.5	15.5	12.0	129	129
18	18.5	16.0	15.0	123	107
16	15.5	18.0	14.5	107	124
14	15.5	18.0	19.5	80	93
12	27.5	22.5	19.5	141	115
10	24.5	24.5	20.0	122	122
8	27.0	26.0	16.5	163	158
6	26.5	27.0	21.0	126	128
4	21.0	27.0	24.0	88	112
2	27.0	29.5	24.0	112	123
38 0	27.0	32.0	23.5	117	136
37 58	28.0	31.5	24.0	117	131
56	27.5	30.0	27.5	100	109
54	32.0	31.0	27.5	116	113
52	30.0	28.0	19.0	158	147
50	28.0	29.0	22.5	124	129

Table II gives the data used in the computation of methyl ether present in sample C. As seen in Fig. 3, some values of the percentage absorption for the cell empty are greater than those for the cell filled with sample C. This is due to the experimental error in each reading. Giving the values in the same order as in Table I, Col. 1 gives the circle setting, Cols. 2 and 3 the absorption percentages for sample C and methyl ether, respectively, and Col. 4 the ratios of the corresponding percentages in Col. 3 to those in Col. 2. The value of the ratio by the method of least squares is 7.9 ± 3.0% and the molar concentration of methyl ether in sample C is 0.20 ± 0.08%. It is thus seen that it is possible but not probable that all of the methyl ether has been removed by washing with concentrated sulfuric acid.

TABLE II

EXPERIMENTAL DATA

1	2	3	4
38 30	2.5	13.5	19
28	5.0	9.5	53
26	1.0	14.0	7
24	3.0	12.0	28
22	0.5	14.5	3
20	2.5	12.0	21
18	0.0	15.0	0
16	0.5	14.5	3
14	0.5	19.5	3
12	3.0	19.5	15
10	3.5	20.5	17
8	−1.0	16.5	− 6
6	0.0	21.0	0
4	1.0	24.0	4
2	3.0	24.0	12
38 0	−3.5	23.5	−15
37 58	2.0	24.0	− 8
56	−1.0	27.5	− 4
54	0.5	27.5	2
52	0.5	19.0	3
50	3.0	22.5	13

Summary

1. A ready method for preparing methyl fluoride pure to within 0.20 ± 0.08% has been described.

2. Quantitative analyses of samples of this gas have been made by high dispersion measurement of the infra-red spectra of the samples, giving probable errors of 0.10%.

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