Analysis of Organic Compounds by Flame Spectrometry. I. Determination of Chlorine in Organic Compounds by Band Spectra of Cuprous Chloride*

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Analysis by flame spectrometric method has developed around metal elements with low excitation energy and recently its application has gradually been extended to heavy metals. On the other hand, determination of nonmetallic elements has been reported only in a few instances, such as the determination of phosphorus[1] and halogen[2] by indirect method, that of the chloride ion in sea water by band spectrum of cuprous chloride[3], that of organophosphorus compounds[4], and semi-quantitative determination of the fluoride ion by photographic measurement[5].

The present writers re-examined the determination of the chloride ion by the band spectrum of cuprous chloride, based on the so-called Beilstein's reaction, developed by Honma and others[3].

It was thereby learned that a stable band spectrum of cuprous chloride can be obtained similarly even in the case of non-ionized chloride and a rapid determination of chlorine in organic compounds was carried out successfully by the use of an organic solvent, *N*, *N*-dimethylformamide (DMF).

Experimental

Apparatus and Reagents.—Measurement of flame spectrum was made with Beckman Model DU spectrophotometer (with 4300 photomultiplier accessory), with 9200 flame attachment, 4020 atomizer burner, and 92300 spectral energy recording adapter. Hydrogen and oxygen were used for excitation. To obtain a stable low pressure hydrogen flow, a combination of a flow meter, a hydraulic pressure governor, and a damper was placed between the burner and the gas regulator. Brief outline of this apparatus is shown in Fig. 1.

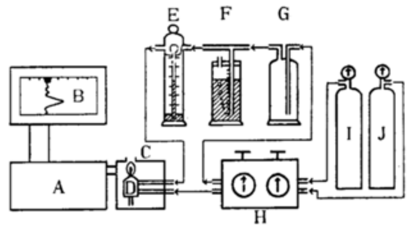

Fig. 1. Schematic diagram of the apparatus.

A	Beckman DU spectrophotometer
B	Spectral energy recording adapter
C	Flame attachment
D	Atomizer burner
E	Flow meter
F	Hydraulic pressure governor
G	Damper
H	Fuel pressure regulator
I	Hydrogen cylinder
J	Oxygen cylinder

The reagents used were all commercial reagents of special grade (G.R. grade). The solvent, DMF was dehydrated and distilled, collecting the fraction of b.p. 152∼153°C. Standard substance for chloride was the γ-isomer of BHC (hexachlorocyclohexane) of standard quality for polarographic analysis.

Experimental Procedure.—*Preparation of the solvent* (Cu, 0.05 M).—In dehydrated DMF, 12.08 g. of cupric nitrate (trihydrate) was dissolved and 1 cc. of nitric acid was added into this solution to prevent the precipitation of cupric hydroxide or basic cupric chloride and the solution was brought up to 1000 cc.

Preparation of standard chloride solution and sample solution.—In a 100 cc. volumetric flask, 4.848 g. of standard BHC (chloride equivalent, 48.48) was accurately weighed and dissolved in DMF containing 0.05 M of copper to prepare standard 1 M chloride solution. The solution was diluted as required to a concentration of 0.05∼0.1 M chloride. Test solutions were prepared by placing a quantity of the sample corresponding to 0.2∼1.0 mM of chloride in a 20 cc. volumetric flask and dissolved in DMF containing copper.

Procedure of flame photometric analysis.—For the analysis, a peak of the band spectrum of cuprous chloride at 435.4 mμ was used and the calibration curve was made from the height of the base line to the peak of the spectral curve.

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[1] W. A. Dippel, C. E. Bricker and N. F. Furman, *Anal. Chem.*, **26**, 553 (1954).
[2] O. Menis, H. P. House and T. C. Rains, ibid., **29**, 76 (1957).
[3] M. Honma, ibid., **27**, 1656 (1955).
[4] O. W. Brite, ibid., **27**, 1815 (1955).
[5] R. Ishida, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **77**, 241 (1956).
* The gist of this work was presented at the 6th Annual Meeting of the Japan Society for Analytical Chemistry in October, 1957.

Conditions of the measurement were as follows: wavelength, 442 to 428 mμ; slit width, 0.05 mm.; sensitivity, full; oxygen pressure, 1.76 kg./cm^2 (25 lb./in^2) on the fuel pressure gauge; hydrogen pressure, 1st, 0.035 kg./cm^2 (0.5 lb./in^2) on the fuel pressure gauge, 2nd, 10 cm. water column; hydrogen flow rate, 450 cc./min.; scanning speed, 10, on the scale of the instrument; chart speed, 7.62 cm./min. (3 in./min.).

Experimental Results and Discussion

Exeitation of Cuprous Chloride Band Spectrum.—The band spectrum of cuprous chloride emitted in oxy-hydrogen flame has bands at the wave lengths listed in Table I[6].

TABLE I. BAND SPECTRA OF CUPROUS CHLORIDE

Wavelength (mμ)	Relative intensity	Wavelength (mμ)	Relative intensity
526.2_3	6	443.3_8	9
498.2_2	2	441.2_4	8
494.6_2	1	435.3_9	10
488.1_5	4	433.3_2	9
484.6_4	3	428.0_9	9
478.8_5	2	425.8_9	7
475.5_7	1	418.7_9	3
449.3_8	5		

The brightest of these is the band at 435.4 mμ, followed by bands at 443.4, 433.3 and 428.1 mμ; 435.4 mμ was taken as the analytical wavelength.

Honma and others have already examined the cuprous chloride band spectrum of a sample in aqueous solution and found that its measured intensity is low and the slit width must be so wide that hardly any fine structures were observed. It was also pointed out that, in this wavelength region, the cuprous chloride band spectrum is interfered by C_2-Swan band owing to the presence of carbon compounds, and does not make quantitative estimation possible.

The present writers, however, were able to overcome these difficulties by weakening the interfering action of C_2-Swan band by careful adjustment of the fuel gas pressure even in the presence of organic compounds and by markedly increasing the intensity of cuprous chloride band spectrum by the use of a suitable organic solvent in place of water.

In general, organic compounds are sparingly soluble in water and the use of an organic solvent will be the only means of preparing a sample solution for flame photometric analysis.

Dimethylformamide as Solvent for Flame Photometric Analysis and Establishment of Measurement Conditions.—Dimethylformamide (DMF) was chosen as the solvent, which dissolves not only many organic compounds, but also copper compounds to an extent of over 17.5% of cupric nitrate (trihydrate), over 15% of cupric chloride (dihydrate), 1.8% of cupric sulfate, and even a small amount of cupric acetate.

When DMF is used as solvent, the fuel gas pressure, especially the pressure and the flow rate of hydrogen, greatly affect the excitation of the objective cuprous chloride and the interfering C_2- Swan band and cupric oxide spectra. At hydrogen pressure of more than 0.14 kg./cm^2 (2 lb./in^2 gauge) the flame becomes very large by inflammation of DMF, attaining a height of over 10 cm., and the emission becomes unstable. The spectral curve obtained in such a case is covered by the C_2-Swan band, cupric oxide and cuprous hydride spectra, and cuprous chloride spectrum are hardly ever distinguishable.

With the decrease of hydrogen pressure, the flame becomes smaller and the effect of interfering spectra lessens gradually, with the appearance of a peak of cuprous chloride band spectrum.

When oxygen pressure is elevated, such as to 1.76 kg./cm^2 (25 lb./in^2 gauge), in order to strengthen the spraying of the sample,

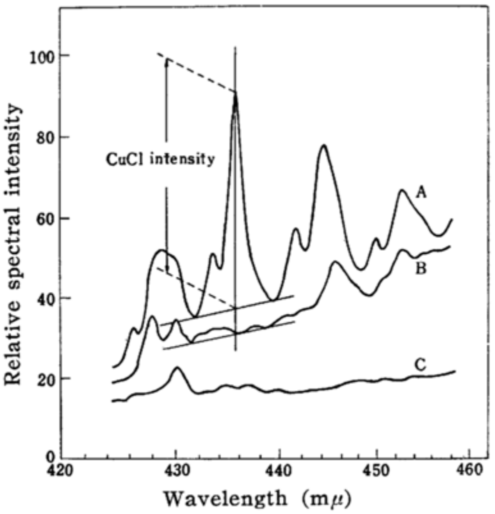

Fig. 2. Spectrum of cuprous chloride.
A (Cu: 0.05 M, Cl: 0.05 M)
B (Cu: 0.05 M)
C (DMF only)
Slit width: 0.05 mm.

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[6] R. W. B. Pearse and A. G. Gaydon, "Identification of Molecular Spectra", Chapman and Hall, Ltd., London (1950).

and hydrogen pressure is adjusted to about 10 cm. water column, cuprous chloride band spectrum gives a distinguished peak, as indicated in Fig. 2.

The slit width was fixed at 0.05 mm., at which the fine structure of cuprous chloride band spectrum can be observed, and the sensitivity was adjusted accordingly. The relationship between the slit width and the cuprous chloride band spectrum is indicated in Fig. 3.

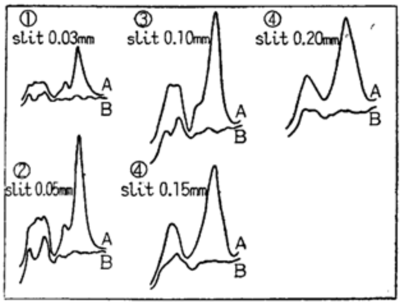

Fig. 3. Effect of slit width on cuprous chloride spectrum.
A (Cu: 0.05 M, Cl: 0.04 M)
B (Cu: 0.05 M)

Preparation of Calibration Curves and Stability of Intensity.—As shown in Fig. 2, a base-line connecting two minima, 431 mμ and 439 mμ, was drawn on a recorded spectral curve, and the height from this line to the top of the peak was taken as the intensity of the cuprous chloride band, whose values were used for preparing the calibration curve.

The concentration of copper affects the stability of the flame and the intensity of the cuprous chloride band and the background. At a low concentration, sufficient intensity can not be obtained; at a high concentration, the background intensity increases and the flame becomes unstable. Examination with various concentrations of copper showed the optimal concentration to be 0.05 M of copper.

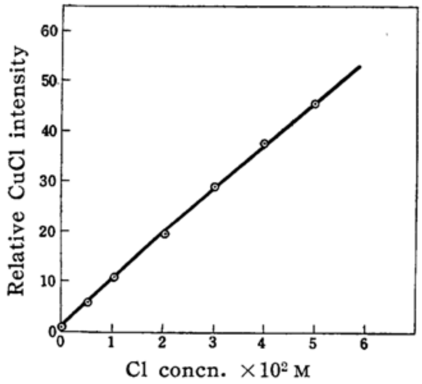

Fig. 4. Calibration curve of chloride.

An example of calibration curve at 0.05 M of copper is indicated in Fig. 4.

In the range of this calibration curve, the intensity becomes most stable in a chloride concentration of 0.02～0.05 M and is available for determination.

Table II gives the stability of cuprous chloride intensity of 0.02 M and 0.05 M chloride concentration.

TABLE II. REPRODUCIBILITY OF CUPROUS CHLORIDE INTENSITY
(concentration of copper: 0.05 M)

Concentration of chloride	
0.02 M	0.05 M
19.8	45.4
19.8	45.6
20.3	45.2
19.5	45.9
18.9	46.1
19.6	45.4
19.9	45.0
19.0	44.9
$\overline{X}=19.6_0$	$\overline{X}=45.4_4$
$\sigma=\pm0.4_4$	$\sigma=\pm0.4_0$

Effect of Moisture.—Sample solution absorbs moisture when left in an open vessel in high humidity and its intensity

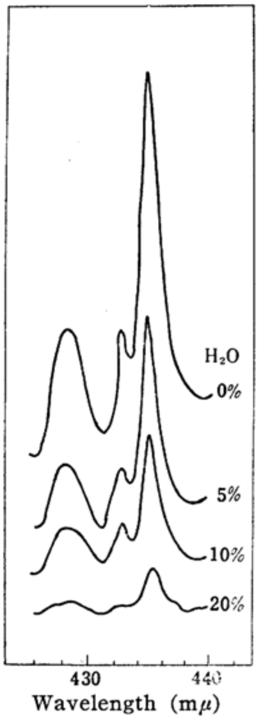

Fig. 5. Effect of moisture on cuprous chloride spectrum.
Cu: 0.05 M, Cl: 0.05 M

TABLE III. DETERMINATION OF VARIOUS ORGANIC CHLORINE COMPOUNDS

Compounds	M.W.	Cl No.	Cl Equivalent	Concn. of Cl (taken)	Concn. of Cl (found)	Recovery %
Chloramphenicol	323.14	2	161.57	0.0257	0.0261	101.5
				0.0398	0.0394	99.0
				0.0514	0.0504	98.1
Monochloroacetic acid	94.50	1	94.50	0.0325	0.0328	100.9
				0.0491	0.0484	98.6
				0.0573	0.0578	100.8
Dichloroacetic acid	128.95	2	64.48	0.0461	0.0469	101.6
				0.0491	0.0501	102.0
Trichloroacetic acid	163.40	3	54.47	0.0237	0.0240	101.3
				0.0418	0.0416	99.6
				0.0474	0.0476	100.5
Chlorobutanol	177.47	3	59.16	0.0227	0.0229	100.9
				0.0454	0.0461	101.6
				0.0428	0.0428	100.0
α-Chloroacetamide	93.52	1	93.52	0.0267	0.0262	98.1
				0.0497	0.0489	98.5
2,4-Dinitrochlorobenzene	202.56	1	202.56	0.0287	0.0290	101.0
				0.0392	0.0380	97.0
				0.0574	0.0582	101.4
Chloramine-T	281.70	1	281.70	0.0237	0.0240	101.3
				0.0338	0.0326	96.5
				0.0474	0.0406	85.6
Procaine hydrochloride	272.77	1	272.77	0.0393	0.0425	108.1
				0.0206	0.0219	106.3
Chloroform	119.39	3	39.80	0.0589	0.0646	109.6
				0.0677	0.0763	112.6
Carbon tetrachloride	153.84	4	38.46	0.0563	0.0725	128.8
				0.0564	0.0717	127.1

will diminish. Hence the determination should be carried out as rapidly as possible after the sample has been transferred to a beaker. The effect of moisture on the spectral curve is shown in Fig. 5.

Determination of Chlorine in Organic Compounds.—Results obtained by the application of the present method to 11 kinds of organic chlorine compounds are shown in Table III.

These results indicate that the amount of chlorine found in solid organic chlorine compounds is approximately 98∼102% of the theoretical value, while the value differs greatly from that calculated for liquid organic chlorine compounds, chloramine-T, and procaine hydrochloride. The values are higer by approximately 30% for carbon tetrachloride, and 10% for chloroform, and very arbitrary for chloramine-T.

Such a discrepancy may be due to the change in the intensity of the cuprous chloride band by the characteristic effect of evaporation rate for carbon tetrachloride and chloroform, by the ionic nature of chlorine of procaine hydrochloride, and by the sodium that forms a salt for chloramine-T. However, further detailed examination is still required.

Range of Application.—It is possible to carry out the qualitative and the quantitative determination of chlorine by dissolving organic chlorine compounds in DMF in a chlorine concentration of over 0.005 M and using 2∼5 cc. of this solution. It is considered possible that this method can be used as a simple procedure for organic elementary analysis.

Organic compounds containing bromine or iodine can also be determined as in the case of chlorine at approximately the same wavelength region but the band spectra of cuprous bromide or cuprous iodide present less intensity than that of chloride under the same condition.

It is hoped that further research will be made on the determination of compounds containing bromine or iodine.

Summary

Examinations were made on the band spectrum of cuprous chloride based on the Beilstein's reaction in oxy-hydrogen flame. Determination of chlorine in organic chlorine compounds was attempted by using dimethylformamide containing

copper as a solvent and a band peak of 435.4 mμ of cuprous chloride.

In order to decrease the effect of C_2-Swan band that is produced on combustion of organic compounds, and to increase the sensitivity of cuprous chloride band spectrum, combustion gas was maintained at high oxygen pressure; 1.76 kg./cm^2 (25 lb./in^2 gauge), and low hydrogen pressure; 1st, 0.035 kg./cm^2 (0.5 lb./in^2 gauge), 2nd, 10 cm. water column.

γ-BHC was used as the standard and determination was carried out on 11 kinds of organic chlorine compounds, and good results were obtained with samples other than liquid, metal salts, and hydrochlorides. The determinable range for chlorine is 0.005～0.1 M concentration.

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