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Gas Chromatographic Estimation of Iron in Air-borne Particulates

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The feasibility of gas chromatographic estimation is reported for iron in air-borne particulates. The particulate is ashed, in an electric furnace, and digested with HNO_3. The acidic digest is neutralized with NaOH, and bufferized with acetate buffer at pH 4.5, and then treated with 0.5% trifluoro-acetylacetone(TFA)-benzene solution to extract iron as Fe TFA chelate. The extracted chelate is submitted to gas chromatography. Some observations have been made on the gas chromatographic conditions.

From environmental and hygienic points, metals found in air-borne particulates have been determined by various instrumental analyses,[2)] while gas chromatography has been hardly used for the purpose.[3)]

Among the metals in the particulates, iron is one of the major components and is known to form metal chelate with β-diketone such as trifluoroacetylacetone (TFA). This chelate has been found volatile enough to enable iron to be determined by gas chromatography with relatively lower column temperature than that for iron acetylacetonate.[4)]

However, the investigation on the application of iron TFA chelate to gas chromatographic analysis of the particulates has not yet been reported. In the author's experiments, it was found that iron was easily extracted with TFA from an acidic digest of the particulate and the formed chelate could be directly gas chromatographed without further pretreatments.

This report offers some observations obtained on the estimation of iron in the particulates by gas chromatography, attempting to see the feasibility of the present method for environmental analysis.

Experimental

Materials——Air-borne particulates were collected by filtering air for 24 hr through a glass fiber filter (Gelman Type A, 9×7 inch) using a High Volume Air Sampler (Staplex) at a rate of 1.42 m^3/min.

Reagents——HNO_3 was of Wako Super Special Grade (SSG) and NaOH, CH_3COOH, and CH_3COONa were of analytical grade. Water was distilled in a glass apparatus. TFA of analytical grade (Dojindo Co., Ltd., Research Laboratories) was distilled under diminished pressure and a fraction of bp 107° was collected on every use. Reagents used for the spectrophotometric study were prepared according to the specifications given in JIS K 0102.[5)]

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1) Location: *a) Takara-machi, Kanazawa; b) Hongo, Tokyo; c) Yayoi-cho, Chiba.*

2) Y. Yamane, M. Miyazaki, S. Kaji, J. Hiromori, S. Kaiho, and M. Ito, *J. Hyg. Chem.* (Japan), **14**, 82 (1968); Y. Yamane, M. Miyazaki, T. Imahashi, S. Bando, Y. Murakami, S. Kaji, and J. Hiromori, *ibid.*, **15**, 238 (1969); Y. Yamane, M. Miyazaki, K. Sakai, T. Imahashi, S. Bando, Y. Murakami, S. Kaji, and M. Ito, *ibid.*, **17**, 387 (1971); Y. Yamane, M. Miyazaki, and H. Nakazawa, *Japan Analyst*, **22**, 1135 (1973); Y. Yamane, M. Miyazaki, and Y. Osada, *J. Hyg. Chem.* (Japan), **19**, 328 (1973).

3) W.D. Ross and R.E. Sievers, *Environmental Science & Technology*, **6**, 155 (1972); M.H. Noweir and J. Cholak, *ibid.*, **3**, 927 (1969).

4) For reviews, see R.W. Moshier, and R.E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Oxford, England, 1965.

5) Japanese Industrial Standard, "Testing Methods for Industrial Waste Water, JIS K 0102-1971," 47. Iron, ed. by Japanese Industrial Standards Committee, JSA, Tokyo, 1971, p. 137.

Apparatus——JGC 750 Type Gas Chromatograph (Japan Electron Optics Co., Ltd.) equipped with a thermoconductivity detector was used. The column was 4 mm (i.d.) × 1 m glass tubing packed with 1% OV-1 on Gas Chrom Z (60—80 mesh). Thermolyne Type 2000 electric furnace was used for ashing the particulates. A glass tube (10 ml volume) with a ground glass stopper was used to extract the iron TFA chelate. Shimadzu-Bausch Lomb Spectronic 20 photometer with glass cell was used for the spectrophotometric measurements.

Analytical Procedure

1) **Preparation of Sample Solution by Extracting Iron from Particulates**——The following procedure was established by partly modifying the method given in the National Air Sampling Network.[6]

Ashing of the particulates was carried out in the electric furnace at 500° for 1 hr, and residue was immersed in 40 ml of HNO_3 (1+1), then refluxed for 1 hr on an electric heater. After refluxing, the mixture was filtered with a glass filter G3 to remove the solid residue. The filtrate was reserved, and the solid residue was retreated with another 40 ml of HNO_3 (1+1) in the same manner. The filtrates were combined and concentrated to 3—4 ml. The concentrate obtained was filled up to 5 ml with distilled water to make sample solution.

2) **Gas Chromatographic Estimation**——One ml aliquot of the sample solution was transfered into a glass tube with a ground glass stopper, and neutralized carefully with solid NaOH and cooled to room temperature. Then, to the solution, 2 ml of acetate buffer of pH 4.5, 1 ml of water, and 2 ml of 0.5% TFA-benzene were added, and the mixture was thoroughly shaked for 3 min on a mechanical shaker. The upper benzene layer was separated, and washed twice with 4 ml of distilled water. The benzene layer was separated and evaporated to dryness and the residue was dried *in vaccuo*. The dried residue was dissolved in a known volume of benzene and subjected to gas chromatographic analysis.

The calibration curve was drawn by using the standard iron TFA chelate, which was synthesized[7] and recrystallized from petroleum benzine (mp 112°) after elution with *n*-hexane on alumina chromatography. Fifty μg/μl of iron TFA chelate benzene solution (Fe 5.42 μg/μl) was prepared and 1, 2, and 3 μl aliquot of the solution was injected into gas chromatograph with the same experimental condition as the sample analysis. The peak area was plotted against the quantity of the chelate. The measurement of the peak area was made by the conventional method both in the standard and the sample.

A calibration curve is shown in Fig. 1.

3) **Spectrophotometric Estimation**——To ascertain the validity of gas chromatography, spectrophotometric method was also applied to the same particulate samples. One tenth ml of the sample solution mentioned above was analyzed by modified spectrophotometry using *o*-phenanthroline described in JIS K 0102.[5] The absorbances of iron *o*-phenanthroline complexes in the sample solution and standard iron solution for making calibration curves were measured at 510 nm.

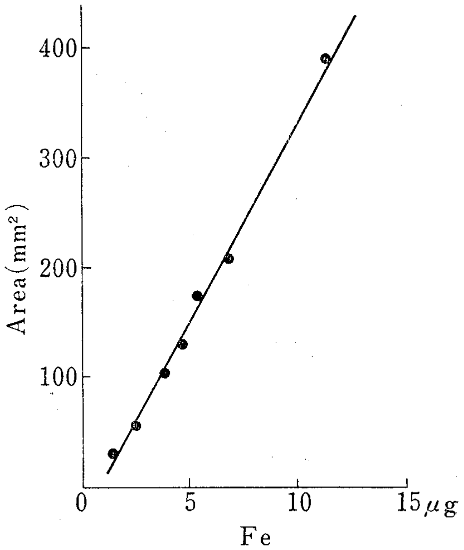

Fig. 1. Calibration Curve

column: 1% OV-1 (Gas Chrom Z, 60—80 mesh), glass, 4 mm φ × 1 m
temp.: column, 118°; detector: TCD, 196°; inject.: 178°
bridge current: 78 mA, carrier gas: He 18 ml/min
attenuation: ×1

Result and Discussion

Extraction of Iron as Iron TFA Chelate

Extraction of iron from aqueous media with TFA was extensively studied by Scribner, *et al.*[8] They reported that 0.5 mmole of iron was quantitatively (99.9%) extracted with TFA from the acetate-buffer solution at pH 4.5 to 5.5 into chloroform layer. In the author's experiment, similar results were confirmed by the spectrophotometric study, and iron TFA chelate was extracted completely with chloroform or benzene. Therefore, TFA benzene solution was used for the extraction of iron from the sample solution for gas chromatography.

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6) U.S. Department of Health, Education and Welfare, "Air Pollution Measurements of the National Air Sampling Network, Analysis of Suspended Particles 1957—1961," ed. by Division of Air Pollution, Washington 25, D.C., Robert A Taft Sanitary Engineering Center, Cincinnati, Ohio, 1962.

7) R.C. Fay and T.S. Piper, *J. Am. Chem. Soc.*, **85**, 500 (1963).

8) W.G. Scribner, W.J. Treat, J.D. Weis, and R.W. Moshier, *Anal. Chem.*, 37, 1136 (1965).

Detector of Gas Chromatograph

A comparative study on detectors of gas chromatograph proved that an ordinary thermoconductivity detector had enough sensitivity for the iron TFA chelate obtained from the particulates and was more preferable than an electron capture detector in easiness of the detector operation for routine analysis. Therefore, a gas chromatograph equipped with a thermoconductivity detector was adopted in this experiment.

Carrier Gas Flow Rate

As for the flow rate of carrier gas, relatively low flow rate was found more preferable than high flow rate for the detection of iron TFA chelate at constant column- and detector temperatures. For example, this observation was clearly seen in the case of He 4 psi (24 ml/min) and 8 psi (80 ml/min) which was shown in Fig. 2.

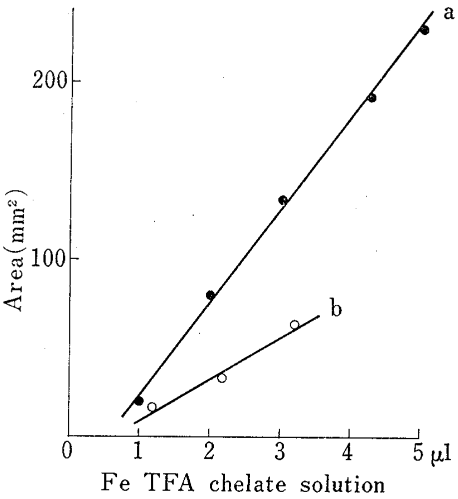

Fig. 2. Gas Chromatographic Behavior of Iron TFA Chelate at Different Carrier Gas Flow Rates

sample: $Fe(TFA)_3$ 25 mg/0.5 ml benzene
column: 1% OV-1 (Gas Chrom Z, 60—80 mesh), glass, 4 mm $\phi \times 1$ m
temp.: column, 104°; detector: TCD, 194°; inject.: 154° bridge current: 70 mA, carrier gas: He a) 4 psi (24 ml/min), b) 8 psi (80 ml/min), attenuation: ×2

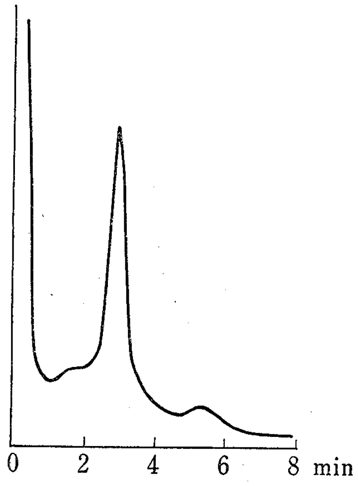

Fig. 3. A Gas Chromatogram of Iron TFA Chelate Obtained from a Air-borne Particulate

sample size: 2.2 μl, taken from 0.05 ml sample solution (benzene)
column: 1% OV-1 (Gas Chrom Z, 60—80 mesh) glass, 4 mm $\phi \times 1$ m
temp.: column, 118° detector: TCD, 196°; inject.: 178°, bridge current: 78 mA, carrier gas: He 18 ml/min, attenuation: ×1

Analyses of Air-borne Particulates

Two different analytical methods, namely, gas chromatography and spectrophotometry were applied for the same two particulates, and the data were compared with each other. Iron contents of the particulate-1, and -2 were 2.9 μg/m³ (the mean of 2.7 and 3.1 μg/m³) and 1.6 μg/m³ (the mean of 1.6 and 1.5 μg/m³) by gas chromatography, and 3.5 μg/m³ (the mean of 3.5 and 3.5 μg/m³) and 1.6 μg/m³ (the mean of 1.6 and 1.6 μg/m³) by spectrophotometry, respectively.

Considering the iron contents obtained by the two methods, gas chromatography proposed here may be concluded to be comparable with spectrophotometry for analysis of iron in the air-borne particulates. A typical gas chromatogram is shown in Fig. 3.

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