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FLOW INJECTION ANALYSIS WITH AMPEROMETRIC DETECTOR UTILIZING THE REDOX REACTION OF IODATE ION

Sanae IKEDA,* Hiromu SATAKE, and Yasuyuki KOHRI
Department of Applied Chemistry, Technical College of
Tokushima University, Tokushima 770

A flow injection method for the determination of oxidizable compounds was developed by utilizing the redox reaction of iodate ion with the sample. Decrease of iodate ion concentration was monitored by measuring its reducing current at a platinum wire electrode held at +0.6 V vs. a silver tubing electrode. Furthermore, L-ascorbic acid, hydrazine and L-cysteine could be determined continuously by using only a hydrazine calibration curve in the concentration range 10^{-4}-10^{-3} mol dm^{-3} with 20 μl samples.

Rapid and sensitive methods for the determination of oxidizable compounds have been studied by the application of flow injection system. In their studies, detection techniques such as spectrophotometry for the determination of hydrazine in boiler feed water,1) potentiometry for L-ascorbic acid,2) amperometry for o-diphenols3) and for isoniazid,4) have been employed.

Present paper describes an application of amperometry for the determination of oxidizable compounds by monitoring the reducing current changes of iodate ion using a platinum wire indicator electrode and a silver tubing reference electrode. Hydrazine, L-ascorbic acid and L-cysteine were chosen for the study as being representatives of oxidizable compounds that react with iodate ion stoichiometrically.

All the chemicals were of reagent grade. Oxygen-free distilled water was used for the preparation of all solutions. Stock solutions (8×10^{-3} M; 1 M = 1 mol dm^{-3}) were prepared from hydrazine dihydrochloride, L-ascorbic acid and L-cysteine monohydrochloride monohydrate, respectively, and standardized by means of amperometric titration5-7) with a potassium iodate standard solution. Sample solutions injected were prepared by further dilution of the stock solutions.

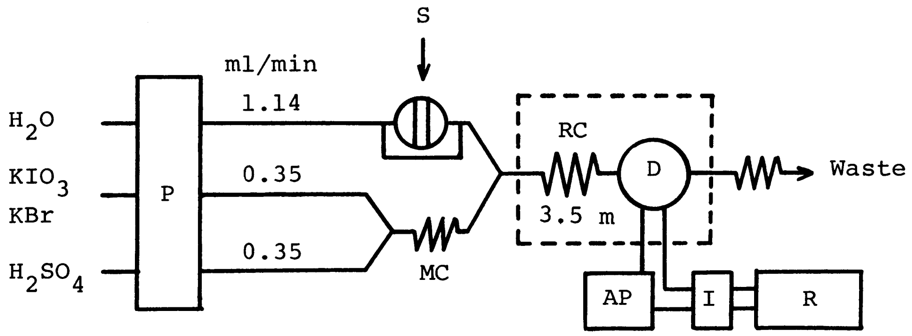

Fig. 1. FIA system for the determination of oxidizable compounds.
P: Peristaltic pump, S: Sample injector, MC: Mixing coil, RC: Reaction coil, D: Detector, AP: Constant voltage-direct current source, I: I-V converter, R: Recorder.

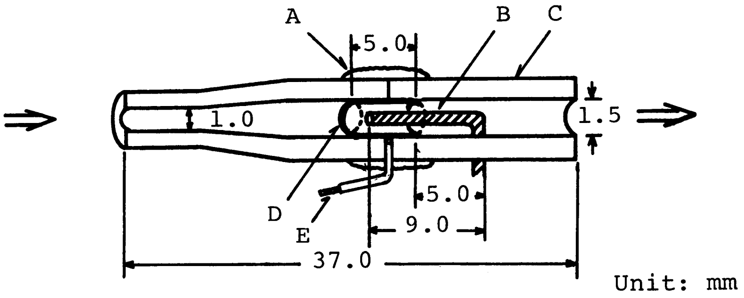

Fig. 2. Diagram of the detector.
A: Silicone rubber, B: Pt-wire, C: Glass tubing, D: Ag-tubing, E: Leading wire.

The system used is shown in Fig. 1. Flows of pure water, H_2SO_4 solution and mixed solution of KIO_3 and KBr were maintained by a peristaltic pump (Gilson, minipulse 2) fitted with Tygon tubings (0.8 mm ID and 1.6 mm ID). The sample injection valve was a Rheodyne Model 7125 with a 20 µl sample loop. All connecting tubing (1.0 mm ID) and mixing coil were of teflon.

Figure 2 shows a diagram of the detector. It was composed of Pt-wire (0.5 mm OD, 9.0 mm long) and Ag-tubing (1.2 mm ID, 5.0 mm long). The potential of Pt-wire electrode (+0.6 V vs. Ag-tubing electrode) was controlled by a constant voltage-direct current source (Takasago, GPH055-2). Reducing current of iodate ion was recorded on a recorder (Toa Electronics, FBR-251A) through a I-V converter (Toa Electronics, PB-130A).

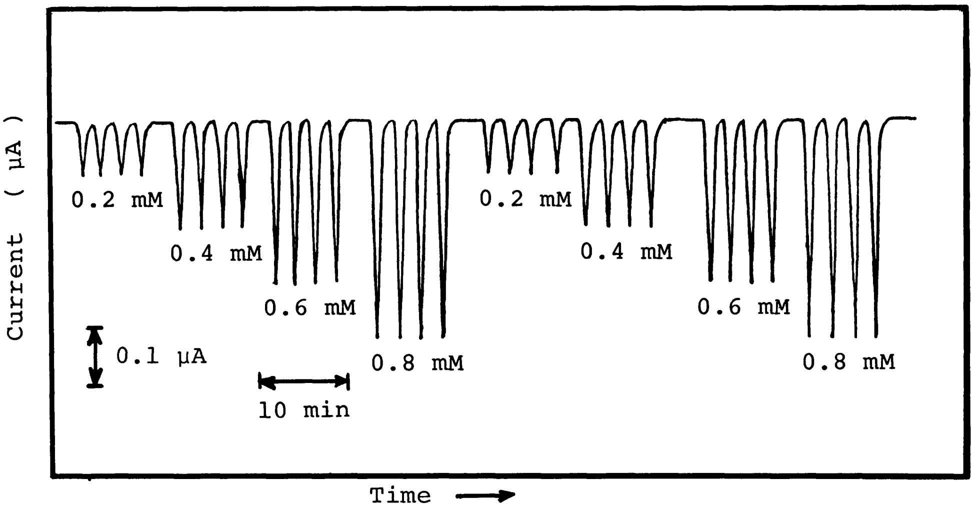

Fig. 3. Calibration runs for the determination of hydrazine dihydrochloride. Sample volume: 20 μl.

Solutions of 10^{-4}M KIO_3-0.42 M KBr and of 1 M H_2SO_4 were pumped at a rate of 0.35 ml/min, and pure water at a rate of 1.14 ml/min. After steady baseline current was attained, sample of 20 μl each was injected at 2.5 min interval via an injection valve, and sharp peaks were obtained.

Typical calibration data are shown in Fig. 3. Calibration curves were linear in the concentration range of $2\text{x}10^{-4}$- $8\text{x}10^{-4}$M for L-ascorbic acid, $2\text{x}10^{-4}$- $8\text{x}10^{-4}$M for hydrazine and $2\text{x}10^{-4}$- $6\text{x}10^{-4}$M for L-cysteine. By using their respective calibration curves, L-ascorbic acid (2.049 μg/20 μl), hydrazine (1.263 μg/20 μl) and L-cysteine (1.045 μg/20 μl) were determined with relative errors of -0.1, +0.2, and -1.7%, and coefficients of variation of 0.7, 0.4, and 0.5%, respectively.

Moreover the slope of the calibration curve was proportional to the stoichiometric molar ratio ($[KIO_3]/[\text{sample}]$) for hydrazine, L-ascorbic acid and L-cysteine (Fig. 4). Therefore the calibration curve of hydrazine can coincide with that of L-ascorbic acid when molar concentration scale for L-ascorbic acid is taken to be a half of the scale of hydrazine. Similarly, the scale for L-cysteine can be drawn to three-halves of the scale of hydrazine (Fig. 5). By using the calibration curve thus obtained, L-ascorbic acid (2.049 μg/20 μl) and L-cysteine (1.045 μg/20 μl) were determined with relative errors of +2.0 and +3.6%.

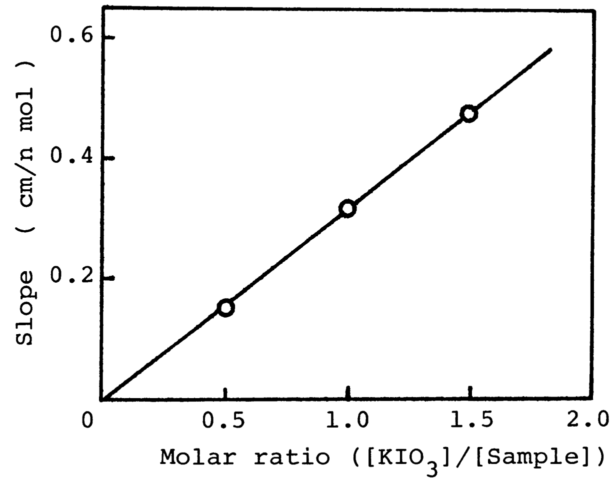

Fig. 4. Relationship between slope of calibration curve and stoichiometric molar ratio.

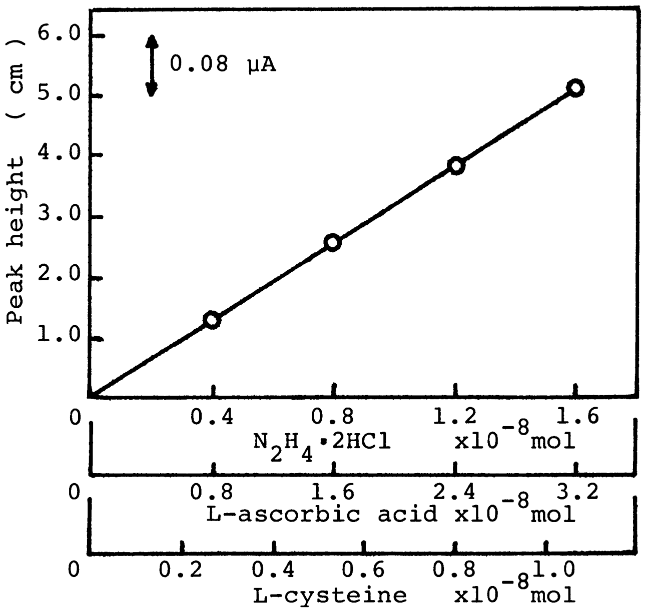

Fig. 5. Calibration curve for hydrazine, L-ascorbic acid and L-cysteine.

By the proposed method, the oxidizable compounds that react stoichiometrically with iodate ion can be determined rapidly, easily and continuously using only one calibration curve obtained by hydrazine solutions.

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