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The Continuous Determination of Filtered Chemical-oxygen Demand with Potassium Dichromate by Means of Flow-injection Analysis

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A useful method, based on the principle of flow-injection analysis, whose flow system is physically analyzed to operate the apparatus, is proposed for the continuous and rapid determination of chemical-oxygen demand (COD) as a dichromate value in organic-waste-water samples. Potassium dichromate in sulfuric acid (1+2) is pumped as an oxidizing and spectrophotometric reagent stream, and D-glucose is successfully used as a standard substance for COD. A redox reaction between potassium dichromate and organic COD substances is carried out at 100 °C in the poly(tetrafluoroethylene) tubing (0.6 mm i.d. × 50 m) of the system. The peaks, obtained at 445 nm in the recordings, show a good reproducibility over a wide range of COD values. A sampling rate of 10 samples per hour is achieved even when the residence time is 30 min. The precision with this method is 1.3%. Chloride up to 200 mg dm^{-3} does not interfere with the determination even if silver or mercury salts are not added.

Of the water pollution which was recognized in Western countries and in Japan during 1970's, chemical-oxygen demand (COD) due to organic substances was the most common. Hence, in Japan, it was decided that the total loads of COD would be regulated from July, 1981, in Japanese water areas having the characteristics of being semiclosed water bodies around which industries and population have concentrated.[1] In this regulation, it was also decided that only the manual acidic permanganate method ($\mathrm{COD_{Mn}}$),[2] cited as a Japan Industrial Standard (JIS), was to be used officially to measure such organic substances. However, the standard dichromate method ($\mathrm{COD_{Cr}}$),[2,3] based on the reduction of a potassium dichromate solution under specific conditions, is ordinarily used to measure such organic substances as the COD value in Western countries. This method is, though, very time-consuming, poisonous, and dangerous because of its complicated manual procedure (*i.e.*, refluxing for 2 h, the use of mercury sulfate, and the use of a concentrated and hot sulfuric acid solutions).

Previously, the present author proposed an idea for the COD measuring apparatus with potassium permanganate using the flow-injection analysis (FIA),[4] a method which was developed by Růžička and Hansen[5] and reviewed by Betteridge.[6] Since then, this apparatus has been utilized in the field of practical analysis of COD values;[7] the apparatus and its derivatives have, for instance, been used for the continuous determination of the COD values ($\mathrm{COD_{FIA\cdot Mn}}$) of various waste-water samples.[8–11] However, the redox reaction with permanganate was essentially incomplete and was variable for the COD determination. Therefore, the FIA method was fairly troublesome for a continuous operation of the apparatus because of a precipitate formation (*i.e.*, manganese(IV) oxide), Hence, to obtain good continuously operating conditions, potassium dichromate should be used as an oxidizing and spectrophotometric reagent for the COD determination by the FIA method, since the redox reaction with dichromate was much more complete and constant than that with permanganate.

This paper will, therefore, describe a version of a newer FIA method with potassium dichromate for the continuous determination of $\mathrm{COD_{FIA\cdot Cr}}$ values in organic, waste-water samples; an improvement of the previous FIA method with permanganate,[4,7–11] reported in this laboratory, by utilizing potassium dichromate in sulfuric acid (1+2) and by analyzing the flow system of the FIA apparatus, and an evaluation of the present FIA method by comparing it with the manual $\mathrm{COD_{Cr}}$ method,[2,3] already optimized as a standard.

Experimental

Reagent. About 3 mol m^{-3} potassium dichromate in a sulfuric acid (1+2) solution was used as an oxidizing and spectrophotometric reagent for a carrier stream. D-Glucose, of an analytical reagent grade, was used as a standard substance for COD.[12,13] Various concentrations of aqueous solutions, the $\mathrm{COD_{Cr}}$ values of which had beforehand been measured by the standard manual method,[2,3] were used to determine the operating conditions of the present FIA apparatus with potassium dichromate.

Apparatus and Procedure. A flow diagram of the apparatus for measuring $\mathrm{COD_{FIA\ Cr}}$ using potassium dichromate developed here is shown in Fig. 1. The apparatus is simply constructed of commercially available parts for high-performance liquid chromatography and poly(tetrafluoroethylene) (PTFE) tubings to give the highest performance.

The potassium dichromate in a sulfuric acid (1+2) solution (A in Fig. 1), which is filtered with a PTFE membrane filter (B) and degassed with a glass degassor (C), is pumped up to the FIA system with a Kyowaseimitsu Model KHU-52, single-reciprocating micro-pump (D) at a pumping rate of 0.6 cm^3 min^{-1}. The two tubes, (a) and (b), are made of 2-mm inner diameter (i.d.) × 0.5-m length and 0.5-mm i.d. × 0.5-m length PTFE tubings respectively. A small volume (*e.g.*, 20 mm^3) of a properly diluted sample solution is introduced just after a line filter (E) through a sample injector with a septum rubber (F) by means of manual injection using a glass syringe. The sample merged with the carrier solution (A) in a reaction tube (c), made of 0.6-mm i.d. and 50-m length, is heated at 100 °C with a Toyoseisakusyo Model VC-250, thermostatted bath using corn oil (G). The resulting solution is transported to a quartz tubular flow cell (I; 10 mm light path and 8 mm^3 inner volume), placed in a Hitachi Model 200-10 spectrophotometer (H), for the absorbance measurements at 445 nm. The absorbances are continuously recorded with time by using a Hitachi Model 056 multirange recorder (J). A 0.25-mm i.d. and 1-m length PTFE tube is placed just after the flow

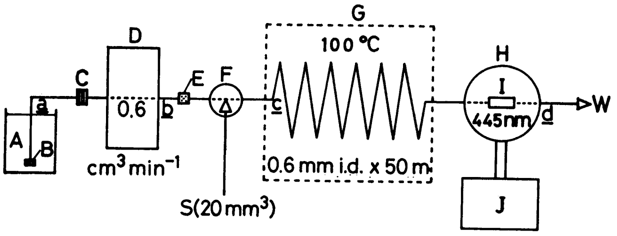

Fig. 1. Block flow diagram of the apparatus for measuring $COD_{FIA\cdot Cr}$ using potassium dichromate. A: 3×10^{-3} mol dm^{-3} potassium dichromate in sulfuric acid (1+2) solution, B: PTEE membrane filter, C: glass degassor, D: single reciprocating micro-pump, E: line filter, F: sample injector, G: thermostatted bath using corn oil, H: spectrophotometer, I: flow cell, J: multi-range recorder, a: PTFE tubing (2 mm i.d. × 0.5 m), b: PTFE tubing (0.5 mm i.d. × 0.5 m), c: PTFE tubing as reaction tube (0.6 mm i.d. × 50 m), d: PTFE tubing as waste line (0.25 mm i.d. × 1 m), S: sample injection (*e.g.*, sample volume: 20 mm^3), W: waste.

cell (I) as a waste line (d) in order to prevent bubbling in the reaction tube (c). The calibration curve is made between the peak areas in the recordings and the manual COD_{Cr} values of aqueous glucose solutions.

Results and Discussion

Choice of a Standard. Considering various organic-waste-water samples, many oxidation reactions have to be examined with regard to many organic substances in the sample solutions. However, D-glucose,[12,13] which has been available as the standard substance for COD, was used to determine the optimum operating conditions of the present FIA apparatus using potassium dichromate.

In the previous FIA method with potassium permanganate,[4,7–11] manganese(VII) was reduced by organic substances (*e.g.*, glucose as the standard) to Mn(II), Mn(III), Mn(IV), *etc.* ions in a sulfuric acid solution. For instance, a black precipitate of manganese(IV) oxide, which had been produced by the redox reaction between permanganate and organic substances, often blocked the PTFE reaction tube of that apparatus. In the present FIA method with dichromate, however, chromium(VI) is quantitatively reduced to Cr(III) by such organic substances, and therefore forms no precipitate in the tube. Hence, the FIA apparatus could be composed of a longer PTFE tubing as the reaction tube, and its continuous operation could easily be achieved for a long time. Moreover, no contamination by organic substances occurred in the tubes of this FIA system because the acidic dichromate solution as a strong oxidant constantly flowed into them.

Design of the Apparatus. With D-glucose as a standard substance for COD, to design the FIA apparatus using potassium dichromate, the effects of such experimental variables as the sulfuric acid concentration, the reaction temperature, the reaction tube (inner diameter and length of PTFE tubing), and the flow rate were examined.

Although a 41.7 mol m^{-3} potassium dichromate in sulfuric acid (1+1) is used as an oxidizing reagent in the standard dichromate method (COD_{Cr}),[2,3] an about 3 mol m^{-3} potassium dichromate in sulfuric acid (1+2) was found suitable as an oxidizing and spectrophotometric reagent for the present FIA method of continuous COD determination because of the high viscosity of sulfuric acid (1+1).

The effect of the temperature on the redox reaction was examined between acidic dichromate and glucose over a long time span (residence time in the reaction tube: almost 30 min). The experiment, controlled with a thermostatted bath using corn oil at 100 °C, was found proper in the case of heating a long-looped PTFE reaction tube. Though the digestion in the COD_{Cr} method[2,3] was carried out for a longer time at a higher temperature (2 h and about 150 °C respectively; see Table 1), glucose was completely digested at 100 °C within 30 min of residence time in this work. However, if large amounts of less oxidizable organic substances than glucose were present in the sample solutions, glucose was not always the best; a more suitable standard substance for COD should be chosen in order to adjust the operating conditions of the FIA apparatus.

The tubing dimensions form one of the most important parameters to minimize the dispersion of the injected sample zone in a reaction tube over a long time span; PTFE tubings of from 0.5 to 1.0 mm i.d. were found usable for the reaction tube of this system. When 0.6-mm i.d. PTFE tubing was, therefore, used as the most promising reaction tube, the effect of the tubing length was examined at 100 °C by using a glucose solution according to the method described in previous papers.[7–10] With an increase in the tubing length, the dispersion of the sample zone also increases in the carrier stream, and so a shorter length is desirable to prevent dispersion. However, the oxidation of organic substances with dichromate is generally slow, so that the redox reaction of the present FIA system at 100 °C requires a longer tubing length. In this work, a suitable length of the 0.6-mm i.d. PTFE tubing was found to be 50 m, since the dispersion severely affected the peak width in the recordings beyond a tube length of 50 m.

The effect of the flow rate of the carrier solution was also examined by using a 0.6-mm i.d. and 50-m length PTFE reaction tube at 100 °C. It was also found that the flow rate should be chosen carefully in order to minimize dispersion over such a long reaction tube. The pumping rate of about 0.6 cm^3 min^{-1} was found the most suitable, and the residence time of the injected sample was about 30 min under these operating conditions.

The degassed carrier solution was pumped up into the FIA apparatus, and then the solution was uniformly heated at 100 °C in the looped PTFE reaction tube. To prevent bubbling of the carrier stream solution, 0.25-mm i.d. and 1-m length PTFE tubing had to be connected as a waste line just after the flow cell in order to obtain back pressure.

The present FIA apparatus using dichromate was, therefore, composed as is shown in Fig. 1. Under these operating conditions, the system was satisfactorily operated at a few atm of back pressure, and no bubble

TABLE 1. COMPARISON OF OPERATING PARAMETERS BETWEEN THE FIA AND STANDARD METHODS FOR COD DETERMINATION

Parameter	FIA method	Standard method
Sample volume	10—100 mm^3	$<$50 cm^3
Reaction medium	H_2SO_4 (1+2)	H_2SO_4 (1+1)
Reaction temperature	100 °C	150 °C (reflux)
Reaction time	30 min	2 h
Detection	Spectrophotometry	Titrimetry (indicator: 1,10-phenanthroline, iron(II) sulfate)
Determination range	50—10000 mg dm^{-3}	10—800 mg dm^{-3}
Masking agent for chloride	None	0.4 g $HgSO_4$+0.33 g Ag_2SO_4
Precision	1.3 %	2.6 %
Sampling rate	10 sample h^{-1}	1 sample (3 h)$^{-1}$
Standard	D-Glucose	None
Reference	This work	2,3

was observed in the recordings. The residence time of the injected sample was almost 30 min, and the oxidation of glucose with dichromate was found not to proceed even when the sample has been stopped in the reaction tube at 100 °C for a further 30 min (the peak area did not change as compared with the case of not stopping the flow).

For reference, the parameters of this method are compared with those of the already optimized COD$_{\text{Cr}}$ method,[2,3] as is shown in Table 1.

Analysis of Flow System. To ensure the operating abilities of the FIA apparatus, the present work provides the following considerations for this useful methodology and this valuable technique.

As the analytical results of fluid viscosity in a laminar flow,[14,15] it has been found experimentally that three distinct stable types of flow, that is, laminar flow without rippling, laminar flow with rippling, and turbulent flow, can be observed in a tube. When the value of the Reynolds number (*Re*) is less than about 2000, the flow is generally laminar. Therefore, it is customary to define the Reynolds number by $Re=D\bar{u}\rho/\mu$, where $D(=2R)$, $\bar{u}$, ρ, μ are the tubing diameter, the fluid average velocity, the fluid density, and the fluid viscosity respectively. Also, the following equation, called the Hagen-Poiseuille law, has been given,[14,15] since the volume rate of the flow (V) is the product of the area (πR^2) and the average velocity ($\bar{u}$):

$$V = (\pi \Delta p R^4)/(8\mu L). \qquad (1)$$

Thus, Eq. 2 is well established for the pressure drop (Δp) in the reaction tube:

$$\Delta p = 32\mu L\bar{u}/D^2. \qquad (2)$$

In the FIA system proposed here, the flow being, of course, laminar (the Re value is calculated to be about 20), the opearting conditions are found to be best fixed as follows: $L=ca.$ 5000 cm, $D=ca.$ 0.06 cm, $\bar{u}=V/\pi R^2=ca.$ 3 cm s^{-1}, and $\mu=ca.$ 0.0013 Pa.[16] Consequently, the proposed flow system can physically be allowed to operate satisfactorily because the calculated Δp value is as reasonable as (but little smaller than) the observed one ($\Delta p=ca.$ 3 atm; measured by means of a Kyowaseimitsu Model KPG-50N pressure gauge) in this work.

The present paper describes a unique FIA method for the COD determination, one which requires a very long residence time and a high temperature for the carrier stream because this reaction attains equilibrium slowly. However, the injected sample was not dispersed so widely to be measured, since the glutinous flow of sulfuric acid (1+2) as the carrier solution was just a laminar flow (Re: about 20) in the present FIA apparatus for COD. The back pressure, which was obtained by means of a thin PTFE waste line (0.25 mm i.d. × 1 m), would also allow the apparatus to be operated at 100 °C.

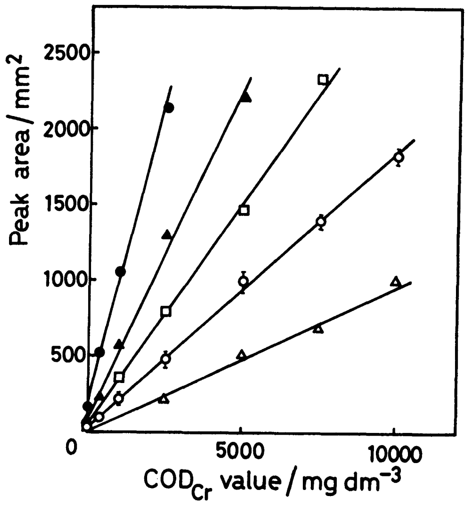

Fig. 2. Calibration curves for glucose.
(△) 10, (○) 20, (□) 30, (▲) 50, and (●) 100 mm^3 of sample solutions are manually injected with a glass syringe.

Calibration Curve and Precision. With the FIA apparatus for COD measurements, peaks at 445 nm in the recordings were obtained with a good reproducibility by using various concentrations of aqueous glucose solutions and by injecting various volumes of the sample solutions. The calibration curves were obtained between the peak areas in the recordings and the COD$_{\text{Cr}}$ values of aqueous glucose solutions for several sample volumes (Fig. 2). The curves can be used as the COD$_{\text{Cr}}$ value for the range of 50—2500, 100—5000, 150—7500, 200—10000, and 400—10000 mg $\mathrm{dm^{-3}}$ when 100, 50, 30, 20, and 10 $\mathrm{mm^3}$ of the aqueous sample solutions are injected respectively. Of course, samples with lower concentrations may be handled whenever a larger volume of the sample can well be introduced into the apparatus. Disappointingly, samples of more than 200 $\mathrm{mm^3}$ were found not to be completely reacted with the carrier solution because of their long sample zones in the reaction tube of this FIA apparatus. The detection limit is, therefore, determined for each sample volume when the increase in the peak area reaches 1.5 times that of the blank peak with distilled water. Accordingly, the detection limits achieved with this method were found to be the $\mathrm{COD_{Cr}}$ values of 50, 100, 150, 200, and 400 mg $\mathrm{dm^{-3}}$ when 100, 50, 30, 20, and 10 $\mathrm{mm^3}$ of sample solutions were injected respectively. The precision of this method was found to be 1.3% in 16 determinations when 20 $\mathrm{mm^3}$ of a 5000 mg-$\mathrm{COD_{Cr}}$ $\mathrm{dm^{-3}}$ aqueous glucose solution was injected into the system. A similar precision could also be obtained for other injecting conditions (sample volume and COD concentration) in this work. Moreover, samples with lower concentrations can also be handled, even by using the same sample volume, when a lower concentration of potassium dichromate is used and detected sensitively and stably.

The reproducibility of the total FIA system was also good, and about 10 samples could easily be analyzed in only an hour with the present FIA apparatus. Figure 3 serves as a representative example of this useful method.

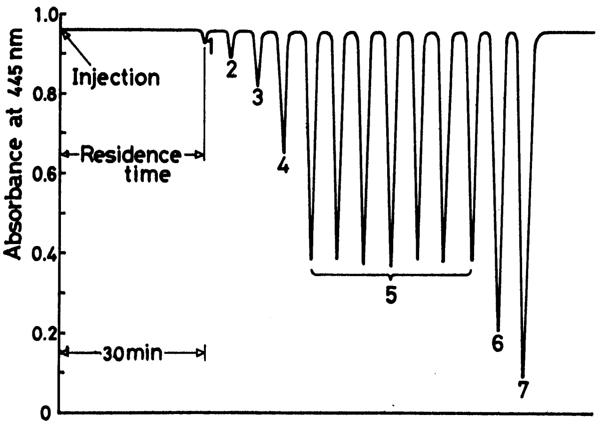

Fig. 3. Typical results of the present FIA for aqueous glucose solutions. 1: 0, 2: 400, 3: 1000, 4: 2500, 5: 5000, 6: 7500, and 7: 10000 mg-$\mathrm{COD_{Cr}}$ $\mathrm{dm^{-3}}$ of sample solutions of 20-$\mathrm{mm^3}$ volume are manually injected with a glass syringe.

Effect of Chloride. To apply this FIA apparatus to actual organic waste-water samples, the effect of chloride was examined in order to evaluate the interference of co-existing chloride ions in the samples with this COD determination. In this work, it was found that chloride essentially interfered with this method, but its interference could be suppressed by adding suitable amounts of mercury and/or silver salts to the FIA system. However, chloride more than 200 mg $\mathrm{dm^{-3}}$ interfered with the determination because of the formation of a silver chloride precipitate, when silver salts (*e.g.*, silver sulfate or nitrate) were added to the carrier reagent solution as a masking agent. As for the results without silver and/or mercury salts, chloride up to 2000 mg $\mathrm{dm^{-3}}$ did not interfere with the determination at a $\mathrm{COD_{Cr}}$ level of 5000 mg $\mathrm{dm^{-3}}$, whereas more than 200 mg $\mathrm{dm^{-3}}$ of chloride interfered with the determination at a $\mathrm{COD_{Cr}}$ level of 400 mg $\mathrm{dm^{-3}}$ when 20 $\mathrm{mm^3}$ of the sample solution was introduced into the system and the injected sample was properly diluted with the carrier-stream solution by dispersion. Hence, these salts were not used as the masking agent for chloride ions in this work, because the inferference of the co-existing chloride ions was relatively small in comparison with the $\mathrm{COD_{FIA\cdot Cr}}$ values of the organic pollutants, as measured with the present FIA apparatus.

Application to Actual Samples. In order to apply this method to various actual organic-waste-water samples, the following experiments are needed for the pretreatment of the sample solutions. Some of the samples used in this work were highly turbid, so the filtration of the samples was first examined. All the samples were filtered with a 0.45-μm pore-size membrane filter; the filtered samples were then placed in the present FIA apparatus for the continuous determination of the $\mathrm{COD_{FIA\cdot Cr}}$ values.

The samples in glass reservoirs were stored in a refrigerator (about 4 °C) as soon as they were sampled, and then filtered. In this storage, the $\mathrm{COD_{FIA\cdot Cr}}$ values obtained for the filtered samples scarcely changed for at least two weeks.

After the above pretreatment steps, various actual samples such as industrial waste water, civil sewage, human waste, and aqueous waste from the laboratory of a university, could successfully be placed in the proposed FIA apparatus, using potassium dichromate for the determination of organic pollutants as COD values. The results obtained are shown in Table 2. By this continuous determination, about 10 filtered samples could semi-automatically be analyzed in only an hour.

Evaluation of Results. The $\mathrm{COD_{FIA\cdot Cr}}$ values found by this method were evaluated by comparing them with the $\mathrm{COD_{Cr}}$ values obtained by the standard dichromate method,[2,3)] as is also indicated in Table 2. Both of the methods gave the same results within a permissible error range from −16 to +13%. Of course, samples such as the waste water of the petroleum industry, which contain much less oxidizable susbtances than glucose, probably show lower $\mathrm{COD_{FIA\cdot Cr}}$ values than the $\mathrm{COD_{Cr}}$ ones. It was also found that no attention was paid to spectral interferences from organic substances absorbing at 445 nm, since the colored organic substances could generally be changed into colorless ones by an acidic dichromate solution at 100 °C because of their strong oxidizability.

The recovery of $\mathrm{COD_{FIA\cdot Cr}}$ was examined by adding known amounts of glucose to the sample solutions before filtration in order to check the results obtained with this method. As a result, it was found

TABLE 2. EVALUATION OF THE RESULTS OBTAINED WITH BOTH METHODS FOR FILTERED COD VALUES IN ACTUAL WASTE-WATER SAMPLES

Sample		$COD_{FIA\cdot Cr}$ (mg dm^{-3})	COD_{Cr} (mg dm^{-3})	$COD_{FIA\cdot Cr}/COD_{Cr}$
Waste water of chemical industry	1	320	360	0.89
	2	780	820	0.95
	3	1700	1600	1.06
Waste water of textile industry	4	1600	1900	0.84
	5	2300	2200	1.05
Waste water of machinery industry	6	910	1050	0.87
Waste water of food industry	7	550	540	1.02
	8	1700	1800	0.94
	9	3600	4200	0.86
Civil sewage	10	270	280	0.96
	11	450	420	1.07
	12	890	950	0.94
	13	2100	2100	1.00
Human waste	14	600	660	0.91
	15	3400	4000	0.85
	16	5900	5300	1.11
Aqueous waste from laboratory	17	80	95	0.84
	18	700	620	1.13
	19	1000	1020	0.98
	20	2600	2500	1.04
	21	2800	3100	0.90
	22	3400	3700	0.92
	23	3500	4100	0.85
	24	5000	4700	1.06
	25	8600	9300	0.92

that these $COD_{FIA\cdot Cr}$ values could accurately be measured by the present FIA apparatus without loss and gain (the recovery of $COD_{FIA\cdot Cr}$ in the examined range is from 98 to 103%).

Conclusion

The simple apparatus described here succeeded in a continuous determination of the COD in organic-waste-water samples. Although the apparatus is not so good in the determination range for common environmental-water samples, this method will improve COD measurement using dichromate (that is, the FIA method has a much more simple procedure and much less personal error than the standard COD_{Cr} method[2,3]). Furthermore, the present FIA method is more simple, stable, reliable, and less troublesome, though less sensitive, than the previous FIA method using permanganate.[4,7-11] Hence, it possesses the following advantages: (i) the use of potassium dichromate as an oxidant causes a reproducible redox reaction with various organic substances for the $COD_{FIA\cdot Cr}$ values; (ii) no precipitate forms in the PTFE reaction tube of the FIA system; and (iii) an FIA apparatus is simply constructed and easily maintained.

This paper also deals with an analysis of the flow system of the present FIA apparatus. To compose an aqueous system which is operated at 100 °C and has a residence time of almost 30 min, a continuous-flow analysis with air bubbles, which is conventionally available by means of a Technicon Autoanalyzer, will be troublesome. However, this FIA method without air bubbles could succeed in minimizing dispersion by selecting the right tubing dimensions and flow rate of the carrier stream over such a long time span. Although the apparatus presented here may not truly be FIA as a rapid determination method, this application extends FIA to a continuous method of COD analysis based on the acidic dichromate value.

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