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REVIEW

CONTINUOUS MONITORING OF POLLUTANTS

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ABSTRACT

An automated continuous monitoring of pollutants such as mercury, phosphor, cyanide and silica is described. The method perform completely continuous and automated on-line monitoring of pollutant in environmental waters. The sample throughput is continuous, while still offering a high analytical performance.

INTRODUCTION

Analytical chemistry plays a dominant role in process control and environmental protection. Improvements in industrial process control are often preceded by developments in analytical chemistry process, which supplies quantitative and qualitative informations about chemical processes.

Industrial hygiene and environmental protection demand possible continuous monitoring of pollutants in order to initiate preventive measures if limiting value are exceeded. Hence the environmental and analytical chemists need suitable methods and instrumentations with appropriate accuracy, reproducibility, sensitivity, selectivity, low cost with the additional feature of fast response.

Two general types of automated continuous flow method are described for this purpose (Varcacel and Luque de Castro, 1987): Continuous segmented flow analysis and unsegmented flow analysis. The segmented flow method, commercialized by "Technicon in the auto analyzer system", correspond to the classical version that was first described by Skeggs in -

1957. Samples are aspirated sequentially, and air bubles separate (segmen) the flow.

The unsegmented flow analysis does not use air bubles as means of separating successive samples. The absence of a gas phase have several advantages (Luque de Castro, 1989) such as shorter lag-phase, higher signal reproducibility, cheaper and less complex instrumentation. The unsegmented flow techniques offers a wide range of possible methodologies. Thus flow injection analysis in its conventional form (normal FIA, injection of sample into a continuous flow of reagent) allows analysis for pollutants with minimum consumption of sample solutions. In casses such as waste water analysis, where the reagents constitute the major cost of the determination, reversed FIA is more suitable. On the other hand, when possible variations in sample compositions necessitate continuous monitoring, an analysis utilizing completely continuous flow (continuous recording of the signal produced) is ideal.

COMPLETELY CONTINUOUS FLOW ANALYZER

Analysis and monitoring of pollutants such as mercury, COD, phosphor, nitrogen, chromium, etc., in the environmental water samples are important. Automated flow methods for these purpose have been described by several groups (Bailey and Lo, 1971; El-Awady *et al*, 1976; Oda and Ingle, 1981; Fang *et al*, 1986; Thomson *et al*, 1983; Hansen *et al*, 1977; Korenaga, 1980; Kuroda and Mochizuki, 1981; Hirai *et al*, 1981; and Kamidate *et al*, 1989). The disadvantages of the batch analyzers are that the instrument is mechanically very complex with many moving parts and each measurement time usually requires about one hour. On the other hand, the conventional flow analyzers based on segmented flow analysis and flow injection analysis have advantage that they are suitable for the analysis of large number of samples and the instrument is less complex. However, all of the conventional flow methods use reagent flow rates at mL/min level and therefore, large amounts of reagent are required for continuous monitoring.

The completely continuous flow analysis (CCFA) was described first by Goto and co-workers (1981, 1983), where the sample was continuously injected as a flowing stream at low flow rate. This is, therefore, a different system from that of segmented flow analysis (SFA) of Skeggs or flow injection analysis (FIA) of Ruzicka and Hansen. Both of which have discontinuities of some sort or another. The schematic comparisson of these three methods (SFA, FIA and CCFA) is shown in Figure 1.

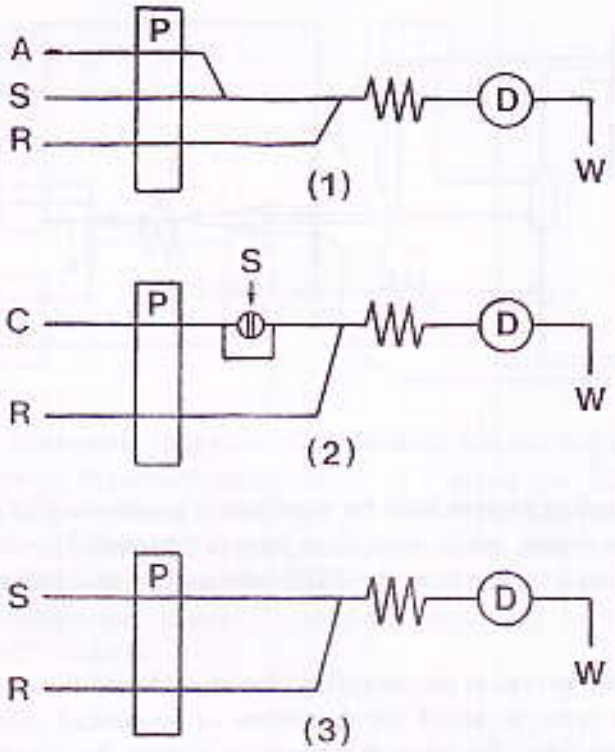

Figure 1. Schematic comparisson between three automatic flow methods. Manifold specifications : 1 = SFA, 2 = FIA, 3 = CCFA, A = air, S = sample, R = reagent, C = carrier, P = pump, D = detector and W = waste.

PROTOTYPE MONITOR

Fast response has been accomplished by speeding up the sample transport or to reduce the distance between the plant or source of contamination and the analyzer (in-site laboratory). The ideal situation, however, would be to directly insert sample into the process stream or effluent which is common practice for monitoring of pollutant. For this reason, the prototype of monitor was constructed and it was installed in the laboratory. The water sample was carried out from a pipe continuously supplying waste water to the laboratory. the construction of sampling system used is shown in Figure 2.

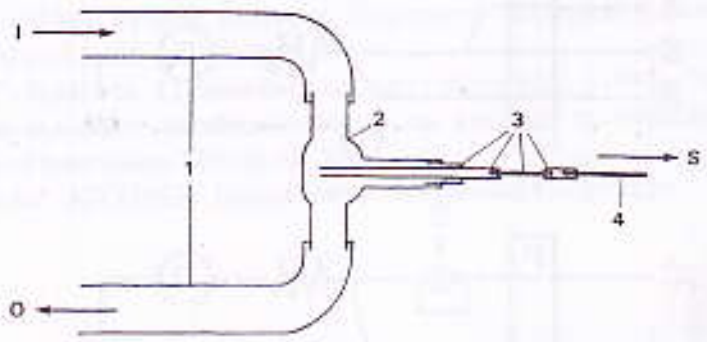

Figure 2. Sampling system used for continuous monitoring of pollutants. I = inlet from waste water pipe, S = sample channel, O = outlet, 1 = polyethylen tube, 2 = glass tube, 3 = PTFE tube and 4 = fused silica.

The waste water arrives at the sampling pipe at moderate flow rate (around 0.5 L/min) in order to avoid the deposition of suspended solid particles inside the glass tube. By using the sampling system describeds above, a continuous monitoring of mercury, phosphor, cyanide and silica in waste water from chemical laboratories were carried out and the results obtained were described below.

MONITORING OF MERCURY

Analysis and monitoring of total mercury in environmental samples are extremely important because of the high tocixi city of mercury and its compounds. Therefore, checking the total content of mercury in waste water from time to time is essential for environmental water control. Automated method for continuous monitoring of mercury, based on completely continuous flow analysis has been reported -previously (Goto *et al*, 1988, Munaf *et al*, 1990a, Munaf *et al*, 1990b). The schematic diagram of the continuous monitoring procedure for total mercury is given in Figure 3. The sample, the mixed solution of oxidizing and catalytic reagent (mixed solution of 2% potassium persulphate and 65 ppm Cu(II) ion, and reducing reagent

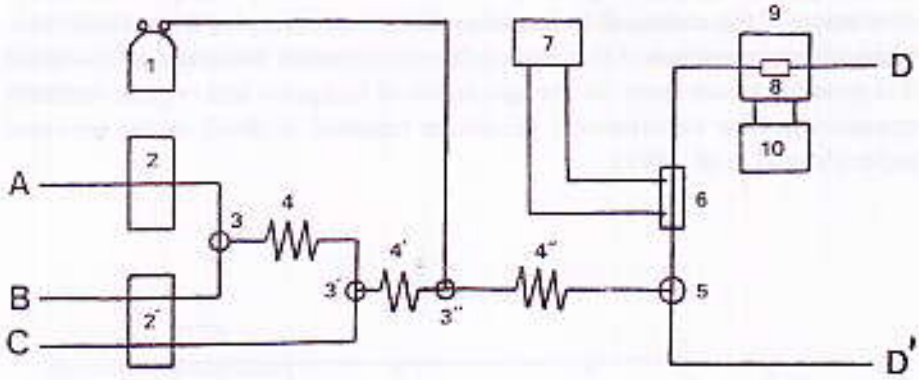

Figure 3. Schematic diagram of continuous monitoring apparatus for total mercury. Manifolds specification : 1 = argon gas; 2,2' = peristaltic pumps; 3,3',3" = mixing joints; 4,4',4" = reaction tubes; 5 = gas-liquid separator; 6 = condenser; 7 = refrigerated circulating bath; 8 = flow cell; 9 = photometer, 10 = recorder; A = sample; B = mixed solutions of potassium peroxodisulphate and copper(II) sulphate reagent; C = tin(II) chloride reagent; D,D' = wastes.

(2 % tin(II) chloride in 3.4 sodium hydroxide) were continuously pumped at the flow rate of 200, 100 and 100 uL/min, respectively. The sample stream was mixed first with the mixed solution of oxidizing and catalytic reagent and introduced into a PTFE oxidation reaction tube (0.5 mm i.d., 27 cm long) without a heating digestion bath. The stream was mixed with the reducing reagent and introduced into a PTFE reduction reaction tube (0.5 mm i.d., 4 cm long), and then mixed with argon gas at a flow rate of 9.0 mL/min. The stream was introduced into a reduction and extraction tube made of teflon tubing (1.3 mm i.d., 60 cm long) and through a laboratory made gas-liquid separator. The mercury vapor produced was swept into the photometric flow cell (40 mm lightpass length and 1.13 mL volume). The absorbance at 253.7 nm was continuously recorded to monitor total content of mercury presence in environmental waters as shown in Figure 4 (Goto *et al*, 1988). The response time for the determination of total mercury was about 4 min, and the detection limit was 0.1 ug/L. The effect of a variety of matrices (cations, anions and organic compounds) in sample was examined and were found to be much smaller than those in conventional automatic methods as described in previous paper (Munaf *et al*, 1989). It is well known that inorganic mercury is converted into the more toxic

methylmercury by aquatic organism. As organomercury(II) compounds such as methylmercury are much more toxic to man than inorganic mercury, speciation of the chemical forms in environmental samples is required. coupling of a microcolumn LC system to the flow system described above make it is possible to use them for the speciation of inorganic and organic mercury compounds. The experimental procedure reported in detail in the previous paper (Munaf *et al*, 1991).

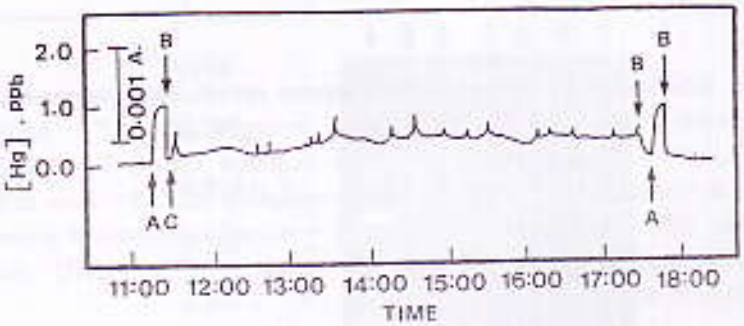

Figure 4. Continuous monitoring of total mercury in waste water from chemical laboratories. Solution pumped : A = standard (1.0 ug/L), B = pure water, C = sample.

MONITORING OF TOTAL PHOSPHORUS

The total phosphorus monitoring in waste water was carried out based on the molybdenum blue reaction (Goto *et al*, 1989). The schematic diagram of the system is given in Figure 5. A sample, an oxidizing reagent and a colouring reagent were continuously pumped with a peristaltic pump at flow rates of 200, 100 and 100 uL/min, respectively. The sample was first mixed with the oxidation reagent of potassium peroxodisulphate and the mixture was introduced into an oxidation reaction tube (0.5 mm i.d., 8 m long) in an aluminium block bath at 140 ^{o}C. A platinum wire (diameter 0.2 mm) was inserted into the reaction tube to serve as a catalyst for the oxidation reaction. The stream was then mixed with the colouring reagent of a mixed solutions of molybdic acid and ascorbic acid. The molybdenum blue formed

was introduced into the photometric flow cell. The absorbance at 880 nm was continuously recorded to monitor total phosphorus present in the waste water sample as given in Figure 6. Coupling of microcolumn LC system with the present system for the speciation of phosphorus compounds is now under progress.

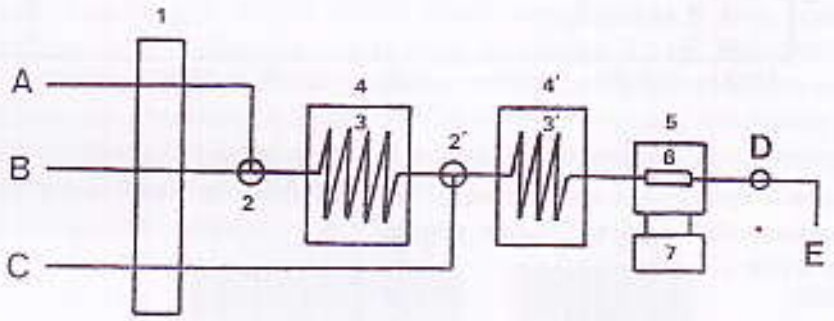

Figure 5. Schematic diagram of continuous monitoring apparatus for total phosphorus. Manifolds specification : 1 = peristaltic pump; 2,2' = aluminium block baths; 3,3' = PTFE tubing; 4,4' = aluminium block baths; 5 = photometer,; 6 = flow cell; 7 = recorder; A = sample; B = potassium peroxo disulphate reagent; C = mixed solution of molybdic acid and ascorbic acid reagent; D = back pressure; E = waste.

MONITORING OF CYANIDE

The completely continuous monitoring of cyanide was descri- bed in detail by Rios *et al* (1984). A schematic diagram for the completely continuous monitoring of total cyanide is shown in Figure 7. Each solutions i.e., buffer solution, chloramine T, pyridine-barbituric acid, and sample was pumped at the same flow rates of 300 uL/min. The buffer solution (pH = 6.3) was mixed first with a chloramine - T reagent and then introduced into a sample stream at the 0.35 mm i.d. and 25 cm long of reaction tube.

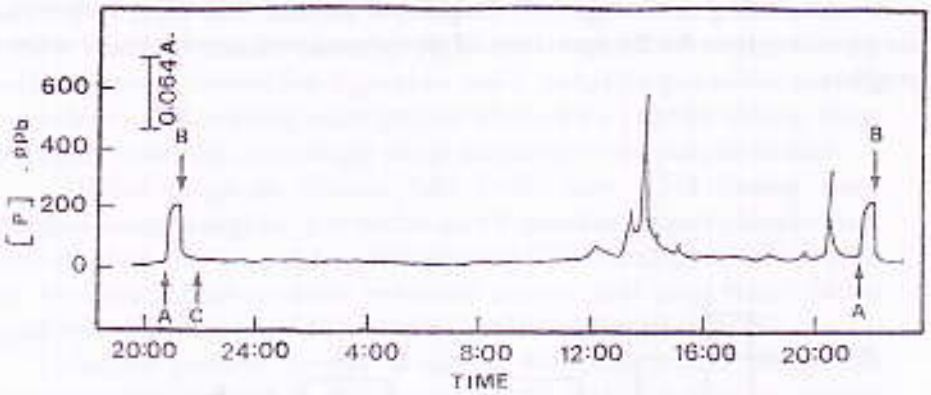

Figure 6. continuous monitoring of total phosphor in waste water from chemical laboratories. Solution pumped : A = standard (200 ug/L), B = pure water; C = sample.

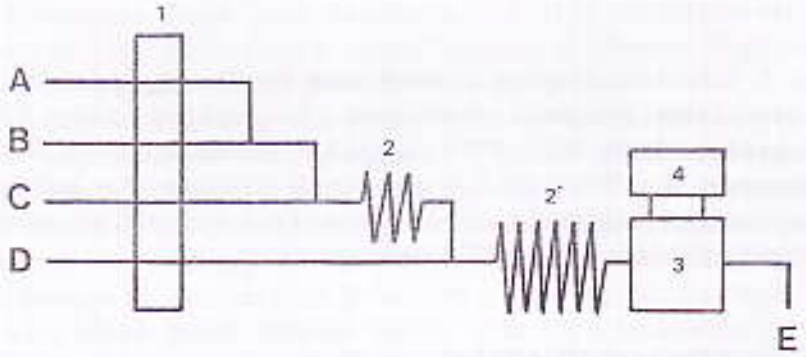

Figure 7. Schematic diagram of continuous monitoring apparatus for total cyanide. Manifolds specification : 1 = peristaltic pumps; 2,2' = reaction tubes; 3 = detector; 4 = recorder; A = buffer solution (pH = 6.3); B = chloramie-T reagent; C = sample; D = pyridine-barbituric acid reagent; E = waste.

The subsequent confluence of the CNCl was mixed with the pyridine-barbituric acid solution and introduced into a reaction tube (0.35 mm i.d.,

525 cm long) at temperature reaction 35 °C. The detectable product, which was violet, was introduced into a photometric flow cell (inner volume 18 uL). The absorbance at 578 nm was continuously monitor the total cyanide present in waste water sample (Rios *et al*, 1984) as shown in Figure 8.

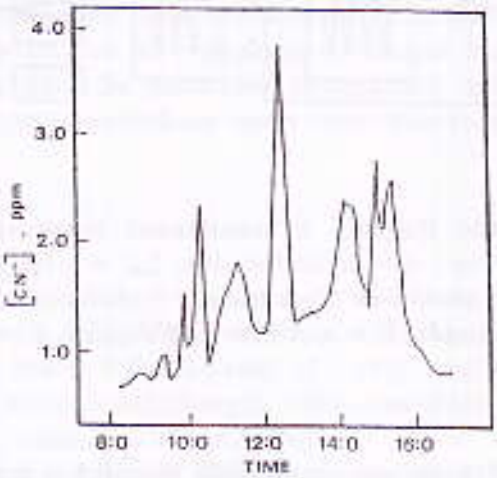

Figure 8. continuous monitoring of cyanide in waste water during a working day.

MONITORING OF SILICA

A schematic diagram for the completely continuous monitoring of trace silicon is shown in Figure 9. The determination was carried out based on the molybdenum blue absorption spectrometry (Goto *et al*, 1989). The sample, a molybdic acid reagent and a reducing reagent (ascorbic acid) were continuously pumped with a peristaltic pump at the same flow rate of 75 uL/min. The sample was mixed with the molybdic acid reagent and then introduced into a PTFE reaction tube (0.5 mm i.d., 8 m long) in aluminium block bath at 23 °C, in which the molybdosilicic acid was formed. A platinum wire with a diameter 0.2 mm was inserted into the reaction tube to assist the mixing of sample with reagent stream. The stream then was mixed with a reducing reagent to form the molybdenum blue, which was then introduced into a spectrometric flow cell (10 mm light pass length, 8 uL volume).

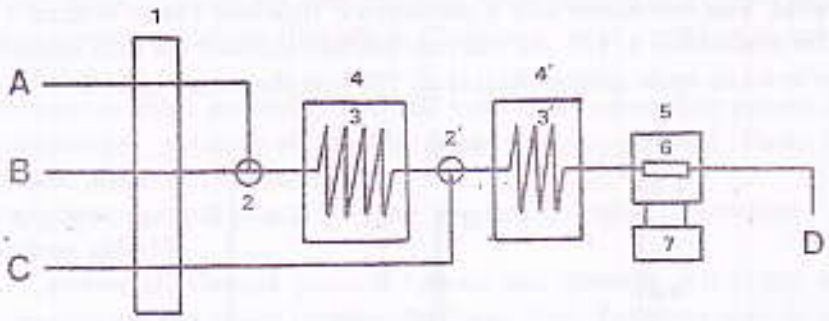

Figure 9. Schematic diagram of continuous monitoring of silica. Manifolds specification : 1 = peristaltic pum; 2,2' = mixing joints; 3,3' = reaction tubes; 4,4' = aluminium block baths; 5 = photometer; 6 = flow cell; 7 = recorder; A = sample; B = molybdic acid reagent; C = ascorbic acid reagent; D = waste.

The absorbance at 815 nm was continuously recorded to monitor the total amounts of trace silicon in sample (Goto *et al*, 1989) as shown in Figure 10.

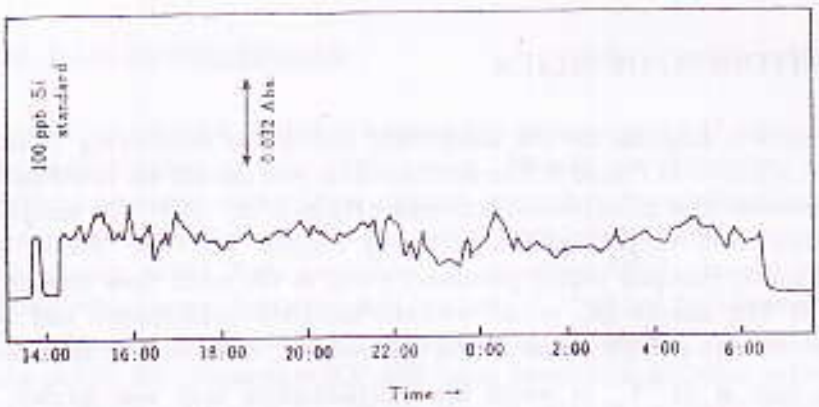

Figure 10. Continuous monitoring of silica in waste water from chemical laboratories. Solution pumped : A = standard (100 ug/L); B = pure water; C = sample.

CONCLUSIONS

The completely continuous flow analysis is a technique which offers the environmental and analytical chemists several advantages. It is fast, simple with a fewer moving parts, accurate and perform completely continuous and automated monitoring of pollutants in environmental waters. The sample throughtput is continuous, while still offering a high analytical performance. Other advantages is that the completely continuous monitoring system is more economic than the automated conventional methods because the amounts of reagents required are much lower than those for conventional analyzers.

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