J. Flow Injection Anal., Vol. 9, No. 1 (1992)

MULTI-CHANNEL WASTEWATER MONITORING SYSTEM FOR PHOSPHORUS BASED ON FLOW INJECTION ANALYSIS

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Certain amount of industrial scale of wastewater is discharged daily from an agricultural organo-phosphorus chemical plant. This wastewater is treated by passage through both activated sludge process and precipitation process with calcium hydroxide solution. To monitor the performance of the treatment systems and to satisfy discharge permit requirements ,hourly analysis of the phosphorus concentration in wastewater is necessary. Currently,orthophosphate species is of main concern. A flow injection analysys(FIA) method developed by Motomizu et al.[1] for determining phosphate in river water seemed applicable for monitoring wastewater in a selected process of the treatment sequence. Very few reports, however,have suggested what kinds of maintenance cares are required to a FIA system to be used for long time in industrial fields.

We have developed the model P-1000 monitoring system,a three-channel wastewater monitor for phosphorus content in phosphate-form. This system was designed for automated operation with limited routine maintenance,i.e. seven days free from maintenance.

This paper reports on field performance,especially troubles caused by long-term use,of the model P-1000 monitoring system which has been operating for eight years in our Ohita Works, since Feburuary 1984.

Experimental

The overall arrangement of the P-1000 system is shown in Fig. 1. For three-channel wastewater monitoring,two sets of automated sample selecting rotary valve with four-way were incorporated in the sampling line. Three real samples were diluted with tap water by means of peristaltic pumps. Six samples including three standard solutions were injected automatically,by means of an automated rotary injection valve with a poly(tetrafluoroethylene) (PTFE) loop through which the selected sample was pumped.

The flow system required two double-plunger and one syngle-plunger micropumps which were used for carrier,color-forming (CF) reagent and acetone. Originally,a set of flow-check tube, filter and gas-liquid separation unit was incorporated in the flow line between the micropump and the reservoir for carrier and CF reagent,but afterwards another filtering unit was added to the flow line of CF reagent. A six-way rotary valve equipped with a nonreturn valve was built in just behind the micropumps,as a means to remove bubbles in carrier and CF reagent. A double-beam spectrophotometer with a flow-cell was used as a detection system. The reaction coil,back-pressure coil and flow lines were made of PTFE tubing. To prevent photochemical reactions,black tubing was used for the line in which CF reagent flowed. The whole system used in the present work was operated under control of a central processing unit (CPU).

Conditions for the measurement of phosphate are shown in Table 1. The model P-1000 system was installed in an instruments room in which temperature is maintained in the range from 22 to 25 ℃.

Results and Discussion

Basic performance of the model P-1000 is the same as that of the phosphate analyzer in our previous work[2]. A calibration curve (absorbance vs. P-concentration) indicates a linear dynamic range of about 500 of magnitude. A determination limit

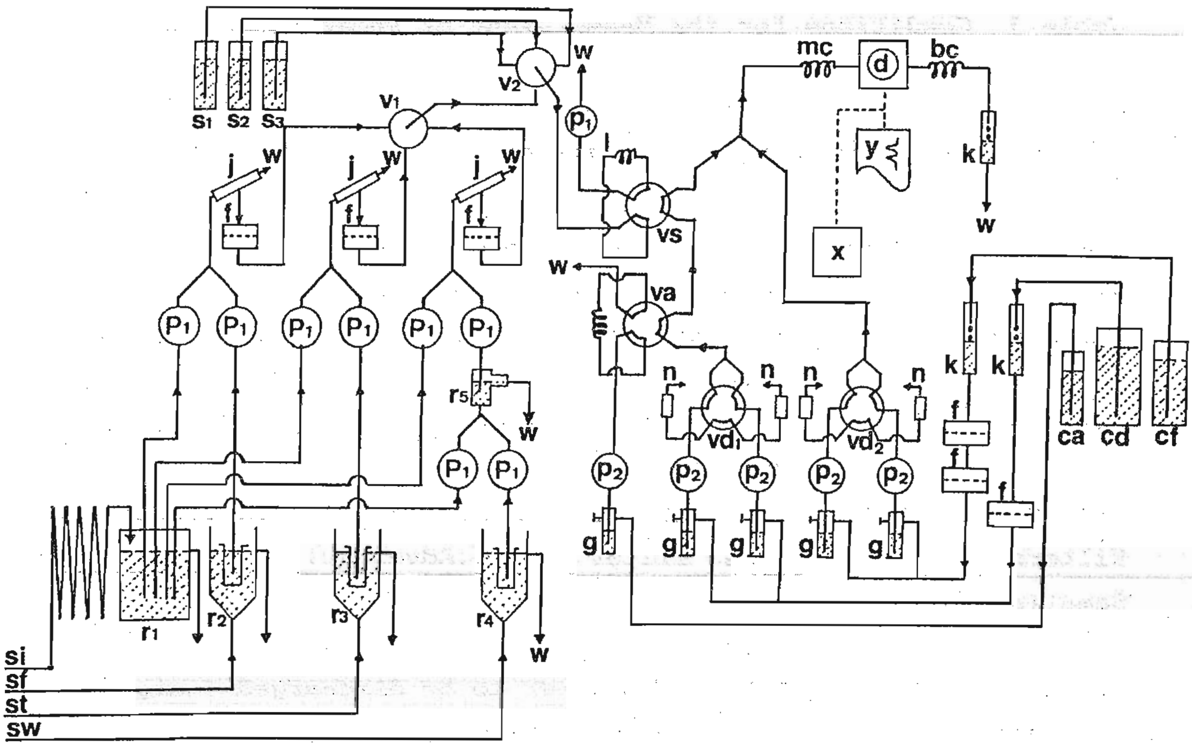

Fig.1 Schematic Diagram of Model P-1000 :bc,back-pressure coil ;ca,acetone;cd,carrier:cf,color-forming reagent; d,spectrophotometer with flow-cell;f,filter;g,gas-liquid separator; j,three-way joint; k, flow-check tube; l,sampling loop;mc,reaction coil; n,nonreturn valve; pl,peristaltic pump;p2,plunger micropump;r1,r2,r3,r4 and r5,reservoirs; s1,,s2 and s3,standard solutions;si,tap water; sf,wastewater to be discharged to river; st,wastewater processed with calcium hydroxide; sw, wastewater from activated sludge process; v1 and v2, rotary valves for selecting sample ; va, rotary valve for washing flow-cell with acetone; vd1 and vd2,rotary valves for removing bubbles; vs,rotary valve for sample injection; x,data processing unit;y,control unit;w,waste.

Table 1 Conditions for the Measurement of Phosphate

	Apparatus:Model P-1000
Pumps for carrier and reagent	Double-plunger micropump (model SP-189, Sanuki Kogyo); 0.1 ~ 2.4 ml/min
Pumps for samples	Peristaltic pump(Master-Flex); 0.5 ~ 20 ml /min
Pump for acetone	Single-plunger micropump(Sanuki Kogyo); 5 ml/min
Flow-check tubes	Glass tube (4 mm bore x 14 cm in length)
Filters	Glass filter (GS-25,Advantec)
Sampling valves	Automated four-way rotary valve (Sanuki Kogyo)
Dilution rates for samples	4 for wastewater to be discharged (sample A),15 for wastewater processed with calcium hydroxide (sample B),and 60 for wastewater from activated sludge process (sample C)
Sample injection	Automated six-way rotary valve (SMV-105, Sanuki Kogyo) with sampling loop of PTFE tube (0.5 mm bore,0.3ml in volume)
Reaction coil	PTFE tube(0.5 mm bore x 5 m in length)
Spectrophotometer	Model S-320-II(Souma Kougaku);tungsten lamp / interference filter(650 nm)
Flow-cell	Made of PTFE;light path 10 mm x 1 mm bore
Back-pressure coil	PTFE tube(0.5 mm bore x 5 m in length)
System controller	Model PC-9800(NEC)
Sequencer	Model SYSMAC-M5R(Tateishi Denki)
Data processing unit	Model Z-80 (CPU ; LH-0080, Sharp Electric) Main memory;ROM 20KB,RAM 16KB
Degital printer	Model DP-310-A(Nippon Denshi Kagaku)
	Reagents

-Table 1,continued-

Carrier	Distilled water (10 liter polyethylene bottle);1 ml/min
Color-forming reagent	0.016M $(NH_4)_2MoO_4$, 2.18 x 10^{-4} M Malachite green, 1.28M H_2SO_4, 25 % ethanol(4 liter polyethylene bottle); 1 ml/min
Dilution water for wastewater	Tap water (Ohita City)
Solvent for washing	Acetone (1 liter media bottle with screw cap)
Standard material	250, 500 and 1000 ng/ml H_2KPO_4(1 liter media bottle with screw cap)
	Monitoring modes
Mode 1(standard)	Every 2 hour / samples A,B and C (refer to "Dilution rates for samples") / AW*
Mode 2	Every 4 hour / samples A,B and C / AW*
Mode 3	Every 2 hour / samples A and C / AW*
Mode 4	Every 4 hour / samples A and C / AW*

* acetone-washing process(5 min)

of 5 P-ng/ml was obtained by optimizing the sample injection volume in the range from 0.25 to 1 ml for given analyte concentration. In the present application,however,the sample injection volume of 0.3 ml was chosen,considering the phosphorus concentration higher than 100 P-ng/ml.

This system has been operated under a CPU control so that the measurement for six kinds of samples are compleated in one hour with five runs for each sample and repeated twelve times a day in the standard measuring mode.

An example of the recordings,obtained around Mar.1991,from the wastewater treatment sequence is shown in Fig.2. Unusual plots in A,B and C on Mar.16 and in B on Mar.28 were found due

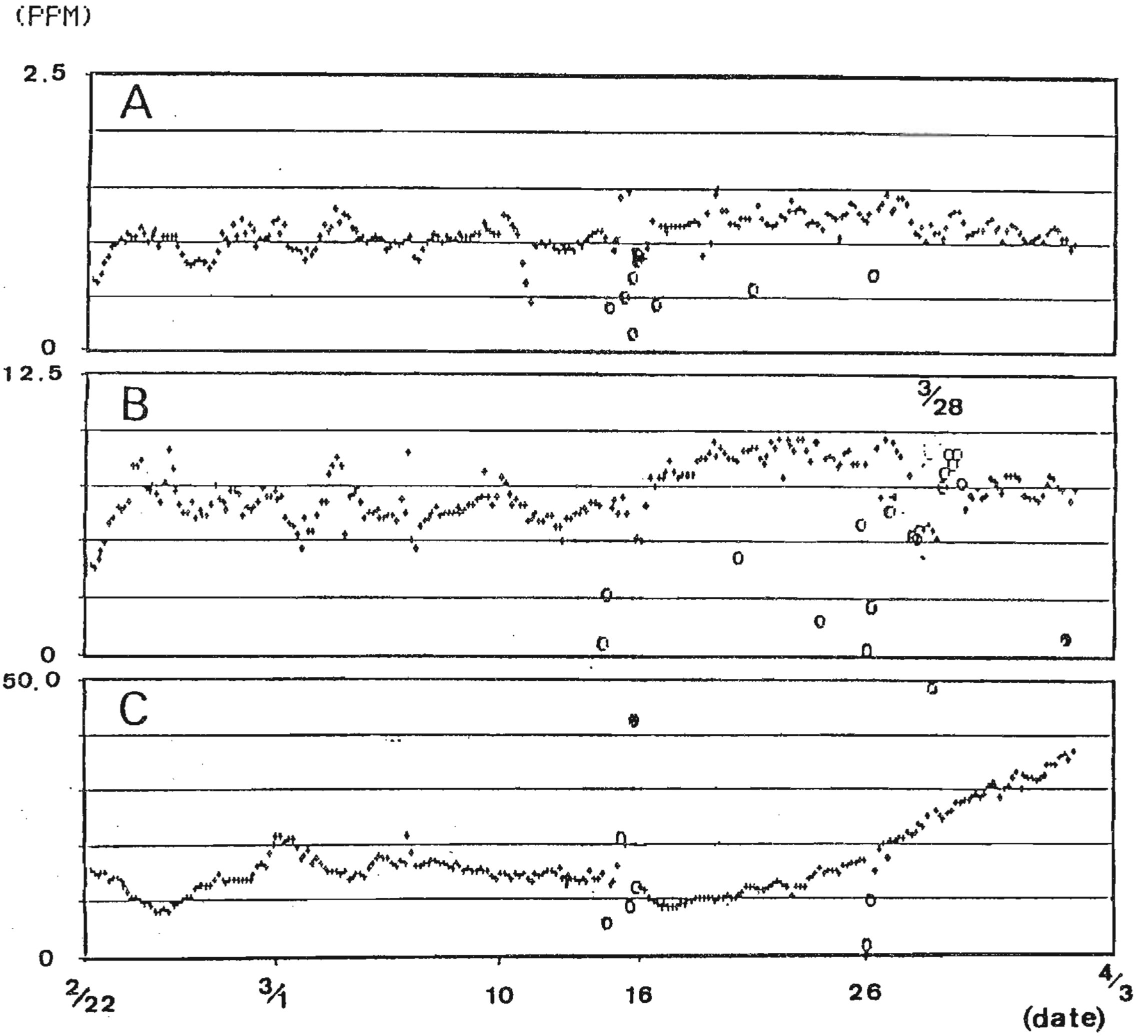

Fig.2 Recordings from Wastewater Treatment Sequence (Depending on the Selecting Valve Position) for Determination of Phosphate. From top to bottom : (A) wastewater to be dischaged, (B) wastewater processed with calcium hydroxide solution,and (C) wastewater from activated sludge process. Symbol(o) represents unusual plot.

to troubles with the micropump for carrier and with the peristaltic pump for diluting sample B with tap water,respectively.

Troubleshooting and maintenance record with the model P-1000 system for the past eight years is shown in Table 2. Judging from the troubles occurred in the first one year,cleaning of

Table 2 Troubleshooting and Maintenance Record

month/ year	trouble or periodical maintenance	troubleshooting or preventive measures
Feb.'84	Model p-1000 system was installed.	
Jan.'85	PTFE tube leading to rotary valve(vd2) for removing bubbles in color-forming reagent was bursted.	PTFE chips plugged up a hole in the valve was removed.
Feb.'85	Irregular baseline drift was observed in connection with revolution of rotary valve(vd2).	The valve(vd2) was replaced. Another filtering unit was built in for increasing capability of removing fine precipitates in color-forming reagent.
	Unstable baseline*	A light source in spectrophotometric detecttion system(d) was replaced.
Mar.'86	Unstable baseline* [Over-voltage(>14v)required due to poor optical alignment resulted in shortening life of tungsten lamp]	The light source in the detection system(d) was replaced. The optical alignment was adjusted.

*normal voltage = 8v

-Table 2,continued-

Nov.'87	Periodical overhauling (1st time)	All of plunger pumps and valves was examined.
Jun.'88	Leakage through a fitting joint in folw-cell (caused by a loosen female fitting)	The flow-cell unit was replaced because of corrosion.
Jul.'88	Unstable baseline. Plunger pump for acetone-washing(p2) was out of order.	A worn-out plunger was replaced.
Jun.'89	Plunger pump for acetone-washing(p2) was out of order.	A gasket was replaced.
	Periodical overhauling (2d time)	Nothing unusual was found.
Aug.'89	Fan for cooling a data processing unit was out of order.	The fan motor was replaced.
Oct.'89	Clock-display was out of order(no movement).	CPU boards for controlling measurement and I/O extension, and IC for clock display were replaced.
Oct.'89	Sample injection valve (vs) was out of order.	The valve motor was replaced.
Nov.'89	Photoelectric switch for automated rotary injec-	The photoelectric switch was repaired.

-Table 2,continued-

	tion valve(vs) was out of order.	
Dec.'89	Parameters stored in data processing unit were out of order(possibly due to electromagnetic noise).	The parameters were stored newly.
Feb.'90	Photoelectric switch for automated rotary injection valve(vs) was out of order.	The photoelectric switch was repaired.
May '90	Motor in automated rotary valve for sampling(v2) was out of order.	The motor was replaced.
Mar.'91	Unusual noise# of motor in plunger pump(p2) for carrier	The motor was replaced. #(caused by abration of bearing)
	Peristaltic pump for dilution was out of order.	The pump was replaced.
Jun.'91	Parameters stored in data processing unit were out of order.	The parameters were stored newly.
Feb.'92	Periodcal overhauling (3rd time)	CPU board for data processing and four fan motors were replaced.

the flow line and elimination of solid particles from both samples and reagents are vitally important to avoid troubles with the rotary valve. The first pump trouble was observed, after about four years use,with the plunger pump for acetone, and a year later,with a gasket of the same pump. Troubles with the motor and the photoelectric switch of the automated rotary valve were observed rather frequently after about six years use. Taking into account that pumps and automated valves are key components of the present monitoring system, emphasis should be placed on preventive measures for deterioratin of those parts.

It is well-known that functions of the integrated circuit is susceptible of exposure to high temperature environment or electromagnetic noise. The first troubles with the clock-display (Oct. '89) seemed to be associated with an anticipating trouble with the fan motor(Aug.'89)resulted in unusual increment of temperatures in the CPU chamber,and the second and third ones with the data processing unit (Dec.'89 and Jun. '91) were possibly due to electomagnetic noise,including thunderbolt.

Any outbreak of algae or microbiologies has not been obseved in the flow lines. This could be attributed to the periodical washing of the flow lines with acetone and to dilution of real samples with tap water to the extent of four to sixty times. That high dilution rates in the later were made practically possible by utilizing Malachite green,which reacts with molybdophosphate in acid medium to form a colored complex with the molar absorptivity of about 1×10^5 $l.mol^{-1}.cm^{-1}$at 650 nm [3], as CF reagent.

Conclusion

A novel multi-channel wastewater monitoring system for phosphorus based on FIA was developed and has been operating for eight years with limited routine maintenance. The field performance of this system proved in the present work indicates that a FIA system,which applications have been confined in analytical laboratories,can provide us with a reliable and versatile means for long-term use in industrial fields.

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(Accepted May 2,1992)