ROBOTICS IN AUTOMATION OF ENVIRONMENTAL WATER ANALYSIS

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Abstract - Chemometrics innovation is now occurring in the field of analytical sciences using an intelligent robot toward laboratory automation. The development activity is depended on the advancement of intelligent robot manipulator in place of the traditional manual procedure of discrete sampling and followed chemical analysis. The system was composed of a Mitsubishi Denki, model RV-M1, robot manipulator, an NEC, model PC9801, personal computer for process control, commercial analytical instruments, and common experimental apparatus improved for the automated procedures. The robotics system could be applied to the automation of chemical oxygen demand (COD) measurement with high precision, reproducibility and reliability, and was found useful for preventing the time-consuming batch chemical/biochemical analyses for purpose of industrial process control and water quality monitoring.

Key words intelligent robot, laboratory automation, process control, environmental water, batch analysis

Recent advances in intelligent laboratory robotics include sophisticated techniques to monitor the progress and reliability of batch chemical analyses[1]. Robotics have often been applied to some pharmaceutical analyses[2-4] since the commercial introduction of the first laboratory robot by Zymark Corp., U.S.A. in 1982. The use of laboratory robots is particularly advantageous when conditions make the work dangerous, hazardous or impossible for humans[5] or when the work is too tedious for humans to perform with sustained accuracy and efficiency[6-8].

Korenaga have been investigated the connection of personal computer with various analytical instruments in laboratory automation[9]. He has recently got his ideas in simple order of automation history for batch chemical analysis procedures as shown in Fig. 1, and then presented an idea of application of the intelligent robot with process microcomputer to tedious batch procedures in water quality analyses based on the official manual method[10,11].

In this paper the authors present an experimental approach of chemometrics engineering utilizing an intelligent robot manipulator in order to apply to the evaluation of wastewater treatment process, industrial process/quality control and laboratory automation. A commercially available robot manipulator is therefore examined to build up an automated procedure for analysis of chemical oxygen demand (COD) which is the most common and important component in environmental water samples. Both the present robotics system and process automation engineering can be applicable to build up the multi-dimensional measurement/monitoring system of multi components for the purpose of water quality evaluation in a given aqueous environment.

EXPERIMENTAL

A basic composition and layout of the intelligent robotics system for COD measurement, is shown in Fig. 2. It is composed of a Mitsubishi Denki, model RV-M1, robot manipulator. an NEC, model PC9801, personal computer for process

Fig. 1 Historical idea for automation of batch chemical analysis procedure by Korenaga[10,11].

control, and commercially available analytical instruments (an automatic conductometric detector, automatic oxidation-reduction potential (ORP) titrator, auto-burets, etc.) and common COD experimental apparatus improved for several automated procedures. An automated experimental procedure for COD measurement using the present robot manipulator is also given in Fig. 3.

Fig. 2 A basic composition and layout of the intelligent robot manipulator system for COD measurement.
 (1) Robot manipulator (Mitsubishi Denki, model RV-M1), (2) personal computer for process control and data processing (NEC, model PC9801), (3) sample table, (4) automatic ORP titrator with an auto-buret for 0.025 N potassium permanganate (Kyoto Denshi, HM-40S), (5) automatic conductometric detector (Kyoto Denshi, CM-40S), (6) auto-buret for sulfuric acid (1+2), (7) auto-buret for 0.025 N sodium oxalate, (8) water bath, (9) silver sulfate powder hopper, (10) magnetic stirrer, and (11) compressed air control unit.

RESULTS AND DISCUSSION

According to the Testing Methods for Industrial Wastewater (K 0102) in Japan Industrial Standards (JIS), various volumes and amounts of reagents and samples were tested by the robot manipulator in comparison with those operated manually in the chemical laboratory, in order to ensure the reproducibility of the pipetting steps with three auto-burets, weighing and adding step of silver sulfate powder, heating step with a water bath, and back titration step with an automatic ORP titrator. After these optimization experiments the robotics automation procedure for acidic permanganate COD method is carried out according to the flow diagram abbreviated in Fig. 3. The addition of silver sulfate was important for both masking of chloride ion and catalyzing non-degradative organic substances. We first developed an automated method for the rapid determination of chloride ion in water samples.

Robot manipulator's work

Fig. 3 A schematic procedure for robotics automation of COD measurement

We have examined about three methods using an automatic conductometric detector, chloride ion selective electrode and turbidimetric titrator, and selected the conductometric detector because of its easy operation and free maintenance property. The weighing step of silver sulfate powder was thus made up by using the automatic conductometric detector for determining chloride ion in sample solutions and direct weighing system from a commercial 500 g glass bottle of silver sulfate powder. The adding step was determined to use 1.0 g silver sulfate powder when less than 0.05 % chloride ion was co-existed. However an adding amount of silver sulfate had to be changed when mixing of sea water generally caused the chloride concentration of more than 0.05 % in the sample water.

The back titration step was also examined in detail after 30 minutes' heating with the boiling water bath at 100 °C and addition of 0.025 N sodium oxalate solution (Fig. 3). The end point detection with the official permanganate indicator method was improved to an ORP electrode method because the spectrophotometric end point detection with a flow-through cell was troublesome in the presence of turbid components in sample solutions. Figure 4 shows a representative ORP titration curve when the excess of the added sodium oxalate solution is back-titrated with 0.025 N potassium permanganate solution. The back titration step was processed by using an artificial intelligence (AI) which was supported with a flexible common expert system. In Fig. 4, the ORP end point detection at 270 mV was found optimum in agreement with a visual permanganate end point which had a little difference from an equivalent point in the ORP titration curve.

The operation properties of the resulting analysis robotics system described here were found much advantageous in view point of practical use having both higher precision (cv. about 0.3 %) than that (cv. 3-5 %) obtained with the official manual method and good reproducibility and reliability based on the proposed intelligent robotics automation. The whole system could be used for COD measurement of 7-8 samples per hour and useful for industrial needs concerning unmanned overnight chemical analyses.

The present robotics system for COD measurement was successfully applied to various industrial wastewater and process water samples. The analytical results obtained had good agreements with those obtained by the official manual method. The regression equation and correlation coefficient with the system were $Y = 0.97X + 0.47$ and 0.993 for 23 COD measurements, when X and Y denoted the COD value obtained with the present robotics and official manual procedures respectively.

With a minor change the basic system for automation of COD measurement can be applied to the batch analysis automation of water qualities such as hexane

Fig. 4 A representative ORP titration curve for 0.025 N sodium oxalate with 0.025 N potassium permanganate and end point detection.

extracts (OILS) and suspended solids (SS) components in various industrial/environmental water samples.

Chemometrics/robotics innovation is now advancing in the field of analytical sciences for industrial process/quality control, water and wastewater treatment/monitoring technology, etc. The development activity of the intelligent robot manipulator system for the manual procedures of the chemical analysis is contributed to the advancement of laboratory automation for discrete sampling and batch chemical analysis. Both the present robotics system and automation engineering are useful for applying to the other environmental water quality analyses and for preventing the traditional chemical and biochemical trace analyses, chromatographic pretreatments, hazardous carcinogenic procedures, etc.

Comparing with the latest laboratory robotics, developed by Zymark Corp.[12], for automation of HPLC pretreatment, membrane filtration and liquid/solution management to build up personal work stations, such the innovative laboratory automation system with a common robot manipulator and personal process computer will accelerate lots of industrial needs for process analytical chemistry in advanced factory automation technology.

The authors greatly thank to Misters S. Yamada of Mitsubishi Gas & Chemicals Co., Ltd., A. Ikeda and T. Yasui of Esuwan Co., Ltd. for their technical discussions and experimental assistance respectively. One of the authors (T.K.) also does a partial financial support given by the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. Advances in Laboratory Automation-Robotics 1986, Eds. J.R. Strimaitis and G.L. Hawk, Zymark Corp. Hopkinton, MA, U.S.A. 1986.
2. S.A. Borman, Anal. Chem., 57, 651A (1985).
3. J.H. Johnson, R. Srinival and T.J. Kinzelman, Am. Lab., 9, 50 (1985).
4. K. Banno and R. Takahashi, Anal. Sci., 7, 511 (1991).
5. P. Bellus, Anal. Chem., 55, 1240A (1983)
6. W.A. Schlieper, T.L. Isenhour and J.C. Marshall, Anal. Chem., 60, 1143 (1988).
7. T.L. Isenhour, S.E. Eckert and J.C. Marshall, Anal. Chem. 61, 805A (1989)
8. R.A. Felder, J.C. Boyd, K.S. Margrey, W. Holman, J. Roberts and J. Savory, Anal. Chem. 63, 741A (1991).
9. T. Korenaga, "Personal Computer in Chemistry" ed. Association of Personal Computer for Chemists, Part 1, p.111, Maruzen, Tokyo, 1984.
10. T. Korenaga, Sanyo Gijutu Zasshi, 39, 1 (1989).
11. T. Korenaga, Kankyo Gijutu, 19, 552 (1990).
12. Instruction Manual, Zymark Bench Mate Series, Nissei Sangyo Co., Tokyo, 1990.