A CONVENIENT MULTI-PARAMETER WATER QUALITY ANALYSIS BY ONSITE FILTERED SAMPLE FOR EUTROPHICATION MONITORING

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ABSTRACT: Ion Chromatography and Flow Injection Analysis systems were integrated by a switching valve. Then, sampling kit was designed by disposable syringe, 0.45um syringe filter, and 2mL plastic vial. 13 water samples were collected from oxidation pond and natural stream in a University campus. Four analytical modes were applied for standard solutions and the environmental samples. The detection limit (S/N =3) in $\mu M/L$ were as follows, SO_4^{2-} (0.31), Cl^- (0.50), NO_3^- (0.89), Na^+ (0.52), NH_4^+ (0.94), K^+ (1.24), Mg^{2+} (0.76), Ca^{2+} (1.75), NO_2^- (0.02), and PO_4^{3-} (0.12), and its EC was 0.03 $\mu S/cm$. Our analytical approach was simple, rapid, low-cost, and multi-parameter that was satisfactory to assess the water samples. Due to the sampling, transportation, storage processes are drastically improved, our approach has potential to contribute to strategic environmental assessment.

Keywords: Flow injection analysis, Ion chromatography, Strategic environmental monitoring

1. INTRODUCTION

Environmental assessment has a multilevel scheme [1][2]. The assessments for environmental acts implementation in the higher planning processes than project level is particularly categorized as strategic environmental assessment (SEA) [1]. Then, the conventional environmental impact assessment (EIA) functions under the SEA at project level [2]. It is clear from the viewpoint of environmental decision- making processes, in the sense, that as one move down the hierarchy from policies, plans, program (PPPs), and then to project, the nature of decision-making has prescribed specifications [2]. There in the water matters, standard methods for water quality analysis [3] have been main technical procedure for EIA under such object specified conditions. On the other hand, even though SEA at higher PPPs process has unique function to enhance more useful problem prospecting and effective environmental programs-projects development [1][2], however the methodologies for suitable water quality monitoring for SEA are still in a development process [4][5]. Hence, technical development for strategic water quality assessment for SEA has been focused on in this study.

Elevated levels of phosphorous in conjunction with nitrogen can negatively affect aquatic ecosystems in many ways in terrestrial fresh water bodies [6][7]. The increased growth of algae and aquatic macrophytes and distinct shifts in species composition are the prominent symptom of eutrophication [8]. These blooms generally contribute to a wide range of water quality problems including summer fish kills, foul odours, and tainted drinking water. Furthermore, certain cyanobacteria produce and release toxins that can kill livestock and may pose serious health threat to humans. To monitor phosphorous and nitrogen concentration of environmental water is important [6][7]. From another viewpoint in general environmental water quality monitoring, the measurement of common anions (SO_4^{2-}, Cl^-, and NO_3^-) and cations (Na^+, K^+, NH^{4+}, Mg^{2+}, and Ca^{2+}) found in environmental water is essential for some environmental waters including rain, lake, underground, and river water [9].

Ion Chromatography (IC) has been recognized to be a very useful approach for the determination of anions and cations, and Flow Injection Analysis (FIA) is also very fundamental for environmental chemistry. Herein an integration of IC and FIA was examined on analysis for phosphorus, inorganic nitrogen ions, other common anions and cations analysis by only one vial of 2mL onsite filtered sample as a convenient multi-parameter water quality analysis.

2. EXPERIMENTAL

2.1 IC-FIA Integration

IC-FIA integration was performed on a TOSOH model IC2010 equipped with the following devices: vacuum degasser, double plunger pump that capacity is 6μL x 2, column oven, auto sampler of capacity 150-300 samples, and conductivity detector (TOSOH, Tokyo, Japan). The integration with FIA was proceeded by modification of merging process of a double plunger pump by installing a 1-2, 3

switching valve (Fig. 1). Applying 1-2 position of the switching valve, eluent from double plunger pumps were merged before sample injector as a conventional IC system. Then, applying 1-3 position of the switching valve, a plunger pump sent carrier and a sample segment was injected into the carrier flowing, and reagent sent by the other plunger pump was merged after the sample injector. Whereas, injected sample and reagent were merged for every 6*uL* alternately.

2.2 Manifold for IC and FIA Analysis

Using, IC mode that was by 1-3 position of switching valve, simultaneous anions and cations separation was carried out using TSK gel Super-IC-A/C (3 *µm* particle size, 0.2 *mequiv./ ml* cationic exchange capacity, 150 x 6.0*mm I.D.*) with conductivity detector. Using FIA mode that was by 1-2 position of switching valve, two channels FIA manifolds were carried out, in which, 2m SAS tube was applied for reaction at 40 *ºC* for EC analysis, and 5.5*m* and 4.0*m* PTFE tube were applied for reaction at 40 *ºC* for NO_3^- and PO_4^{3-} analysis, with 540*nm* and 660*nm* spectrophotometric detector, respectively.
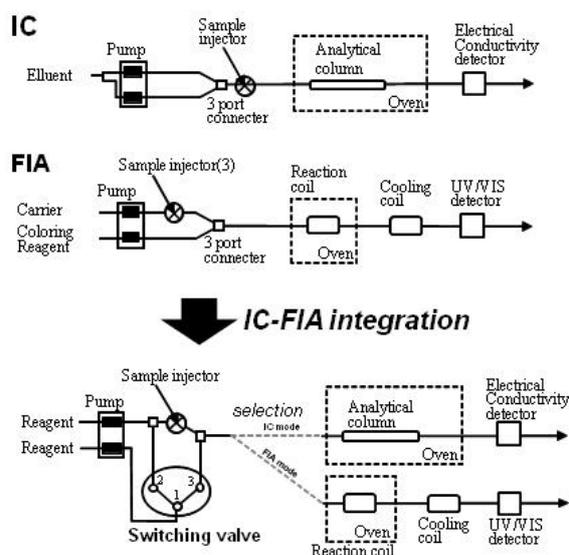

Fig. 1. Schematic depiction of IC and FIA system, and its integration by a switching valve.

2.3 Chemicals and Analytical Conditions

All reagents used in this study were analytical-reagent grade purchased from Sigma Aldrich and Merck, and ultra pure water system (Millipore Direct Q3) was used to prepare standard solutions, washing solvents and eluents. Analytical balance, ATY 224 (Shimadzu, Tokyo, Japan) was used to balance reagents.

Common Anion and Cation analysis: A stock solution of Na_2SO_4, KNO_3, NH_4NO_3, and $MgSO_4$,

and a different $CaCl_2$ solution were solved to 0.1*M/L*, respectively. These two stock solutions were mixed with the ultra pure water for calibration purpose for common anions and cations simultaneous analysis. 10*m M/L* tartaric acid with 3m *M/L* 18-C-6 was prepared for eluents [10]. Flow rate was 1.0 *mL/min*, injection volume was 50µL, and duration of an analysis was 7.5*min*.

NO_2^- analysis: $NaNO_2$ (0.069*g*) was dissolved into 50*mL* ultra pure water as a 20m*M/L* stock solution, and mixed with the ultra pure water for calibration purpose. Concentrated hydrochloric acid (12*M/L*, 417*µL*) was diluted into 50*mL* ultra pure water as a 0.1*M/L* HCl solution. Sulfanil amide (0.5*g*) was dissolved into 50*mL* 0.1*Mol/L* HCl as reagent solution A, and N-(1-Naphthyl)ethylene diamine dihydrochloride (0.05*g*) was dissolved into 50*mL* ultra pure water as reagent solution B. The reagent solution A and B were mixed just before analysis as coloring reagent for FIA to analyze NO_2^- [11]. Flow rate was 0.25 *mL/min* x 2, injection volume was 50µL, and duration of an analysis was 3*min*.

PO_4^{3-} analysis: KH_2PO_4 (0.06804*g*) was dissolved into 50ml ultra pure water as 0.01 *M/L* stock solution, and mixed with the ultra pure water for calibration purpose. Ammonium molybdate (0.274*g*), antimony potassium tartrate (0.0125*g*), concentrated sulfuric acid (3.35*mL*), L-ascorbic acid (1.5*g*), and sodium dodecylsulfate (0.05*g*) were dissolved into 50*mL* ultra pure water as coloring reagent [12]. Flow rate was 0.5 *mL/min* x 2, injection volume was 50*µL*, and duration of an analysis was 3*min*.

EC analysis: 0.1 *mM/L* KCl was used for 147*µS/cm* standard solution for EC at 40*ºC*. Flow rate was 1.0 *mL/min*, injection volume was 50*µL*, and duration of an analysis was 3*min*.

2.4 Field Sampling

13 environmental water samples were collected to each of 2mL plastic vials by onsite filtration (0.45 *µm* nylon syringe filter). Sampling locations were where groundwater discharging from a cut slope beside a road (*S*1), forested upstream (*S*2-*S*3) and its downstream of developed campus area (*S*4-*S*6), and discharge from the campus (*S*7), and oxidation pond (*S*8-*S*13) that discharge to river between *S*5 and *S*6 in UTM Johor campus. These are representing human impacted water environment. The sampling was performed of 12:00 to 13:00 on 24 Feb. 2012.

3. RESULTS

Calibration graphs were obtained by plotting peak area against the concentration of standard solutions. Linear calibration graphs (r^2>0.999) were

obtained for anions and cations simultaneous analysis in the concentration range 0-0.8mM for common anions (SO_4^{2-}, Cl^-, and NO_3^-), 0-0.4mM for cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}), 0.0002-0.025mM for NO_2^-, 0.00005-0.05mM for PO_4^{3-}, and 0.005-2.0mM (7.35-2940 $\mu S/cm$) for KCl.

The detection limits determined at a signal-to-noise ratio of three were 0.31 $\mu M/L$ for SO_4^{2-} (29.5 ppb), 0.50 $\mu M/L$ for Cl^- (17.7 ppb), 0.89 $\mu M/L$ for NO_3^- (12.5 ppb), 0.52 $\mu M/L$ for Na^+ (11.9 ppb), 0.94 $\mu M/L$ for NH_4^+ (13.2 ppb), 1.24 $\mu M/L$ for K^+ (48.5 ppb), 0.76 $\mu M/L$ for Mg^{2+} (18.4 ppb), 1.75 $\mu M/L$ for Ca^{2+} (70.0 ppb), 0.02 $\mu M/L$ for NO_2^- (0.7 ppb), 0.12 $\mu M/L$ for PO_4^{3-} (11.4 ppb), and 0.03 $\mu S/cm$ for EC (Table 1).

4. DISCUSSION

In this study, common anions and cations simultaneous analysis for SO_4^{2-}, Cl^-, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} were performed by IC mode. Then the analytical resolution was satisfactory and can be considered useful for the accurate determination of these common anions and cations. Moreover, the analysis is a part of an advanced non-suppressor type IC by "polyacrylate–based weakly acidic cation-exchange resin column" with weak-acid eluent [13][14]. By the analytical column, a series of very functional water quality analysis are obtained, such as, these 8 ions plus

Table 1. Water quality of stream water in Univeristy Teknologi Malaysia on 24 Feb. 2012.

		SO_4^{2-} [uM/L]	Cl^- [uM/L]	NO_3^- [uM/L]	Na^+ [uM/L]	NH_4^+ [uM/L]	K^+ [uM/L]	Mg^{2+} [uM/L]	Ca^{2+} [uM/L]	NO_2^- [uM/L]	PO_4^{3-} [uM/L]	EC [uS/cm]
S1	Groundwater discharging from cut slope	14.7	124.1	18.8	111.9	3.6	3.8	45.3	61.6	2.4	0.190	344.9
S2	Natural stream in forested area	4.6	68.6	6.3	79.1	2.6	5.7	52.5	72.5	0.2	0.174	292.4
S3	Nagural stream after small human effect	15.3	93.5	15.4	105.8	2.7	8.5	45.4	79.4	0.8	0.183	358.2
S4	Up stream, open water	14.1	77.4	8.8	93.7	2.6	7.5	96.2	165.6	0.2	0.207	554.1
S5	River, upstream of oxdation pond	36.9	109.5	3.0	130.2	1.2	17.8	33.6	200.7	0.2	0.168	594.6
S6	Downstream of oxdation pond	108.5	287.9	9.9	259.0	119.3	43.5	36.3	292.1	0.9	0.280	1166.6
S7	River, infront of security gate	110.2	311.0	19.0	263.3	111.8	50.4	37.3	294.4	1.6	0.620	1206.0
S8	Oxdation pond (NE)	160.4	404.3	9.2	318.0	143.4	58.5	40.0	315.9	2.0	0.348	1451.8
S9	Discharge from oxdation pond	157.2	428.8	11.5	352.5	235.9	61.4	37.6	327.9	0.9	0.504	1641.2
S10	Oxdation pond (NW)	155.3	454.1	6.4	371.3	227.0	65.7	34.9	314.1	0.5	0.541	1610.5
S11	Oxdation pond (SE)	167.0	481.9	6.8	379.7	255.6	70.1	32.9	315.5	0.2	0.696	1720.7
S12	Oxdation pond (SW)	174.6	517.1	7.9	404.6	360.5	78.4	37.8	352.9	0.2	7.340	2022.1
S13	Inflow water to oxdation pond	213.4	689.0	12.9	592.8	416.5	91.9	40.6	360.4	1.7	22.364	2490.9
	Environmental sample data (max)	213.4	689.0	19.0	592.8	416.5	91.9	96.2	360.4	2.4	22.4	2490.9
	Environmental sample data (min)	4.6	68.6	3.0	79.1	1.2	3.8	32.9	61.6	0.2	0.2	292.4
	Caribration graph range (max)	400	400	400	400	400	400	400	400	25	50	2940
	Caribration graph range (min)	0	0	0	0	0	0	0	0	0.2	0.05	7.4
	Detection Limit*	0.31	0.5	0.89	0.52	0.94	1.24	0.76	1.75	0.02	0.12	0.03

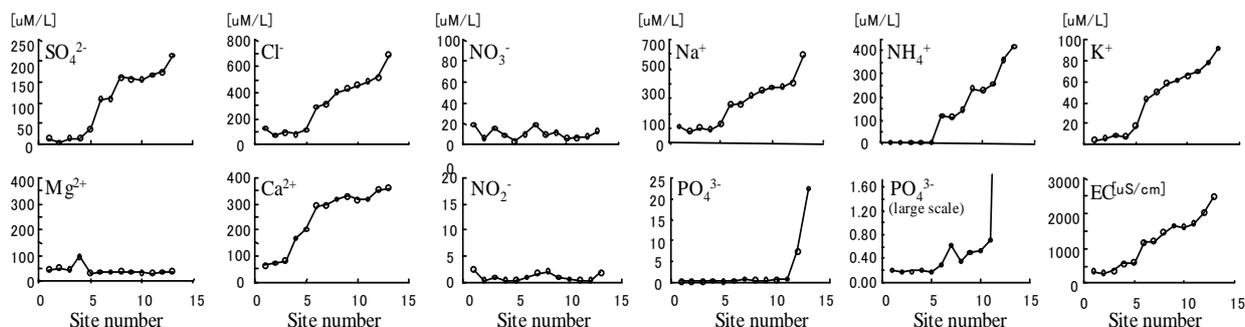*: The detection limits determined at a signal-to-noise ratio of three.

Fig. 2 Water quality of stream water in Universiti Teknologi malaysia on 24 Feb. 2012. Comparing to detection limit shown in table 1, the resolution among analyte anions, cations, and EC were quite satisfactory, and the methods were useful for the accurate determination of these parameters in common river water.

As shown in Table 1, the water quality of stream water were ranging 4.6-213.4 $\mu M/L$ for SO_4^{2-}, 68.6-689 $\mu M/L$ for Cl^-, 3.0-19.0 $\mu M/L$ for NO_3^-, 79.1-592.8 $\mu M/L$ for Na^+, 1.2-416.5 $\mu M/L$ for NH_4^+, 3.8-91.9 $\mu M/L$ for K^+, 32.9-96.2 $\mu M/L$ for Mg^{2+}, 61.6-360.4 $\mu M/L$ for Ca^{2+}, 0.2-2.4 $\mu M/L$ for NO_2^-, 0.2-22.4 $\mu M/L$ for PO_4^{3-}, and 292.4-2490.9 $\mu S/cm$ for EC (Table 1). Comparing to detection limit shown in Table 1, the resolution among analyte anions, cations, and EC were satisfactory in order to assess the trend of environmental water quality difference in UTM campus (Fig. 2).

PO_4^{3-} and SiO_4^{2-} simultaneous analysis[15], HCO_3^- analysis[16], simultaneous heavy metal analysis for Ni^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, and Cd^{2+} [17]. Applying this advanced IC, there is a potential to develop integrated IC for common cation and anion, nutrients, and heavy metals by only one analytical column and equipment.

However, some important parameters, for example COD, total nitrogen (TN), total phosphorous (TP) are impossible to analyze by conventional IC, and generally seawater samples are not applicable for IC. In addition, some parameters,

for example IC for phosphorous has low sensitivity for environmental monitoring [15]. On the contrary, FIA has advantage for these analyses [11][12][18][19]. Accordingly, because of similarity in system design between IC and FIA, these analytical systems were integrated in this study (Fig. 1). Consequently, SO_4^{2-}, Cl^-, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, NO_2^-, PO_4^{3-}, and EC were able to be analyzed from only 2*mL* onsite filtered sample in a plastic vial. This multi-parameter analysis can be extended to TP [12], TN [18], COD [19], HCO_3^- [16] within another one 2*mL* vial sample, easily, and the analytical capacity is several hundred samples regarding the capacity of auto sampler of IC2010.

In order to embark on effective environmental restoration programs and projects, SEA is quite important [1], where new methodologies for SEA need to be developed [8][9]. According to literature [8][9], expected properties of such new approach is "rapid delivery of results, on-site, low-cost, and capacity to acquire large number of observations within a short time frame". Regarding the requirement, the concept of on-site analysis was eliminated, and time frame for rapid delivery of result is assumed as one day, and then, convenient experiment procedure, satisfactory accuracy, capacity of automated large number sample analysis, and integrated multi-parameter analysis were of more concern in this study. According to our analytical approach, because of reduction of sample volume, even the concept of onsite analysis was eliminated, field sampling process and sample transportation process were drastically improved, and then, convenient and enough accuracy of multi-parameter large number sample was available, which will contribute to SEA as a new technical approach that improves problem recognition processes in environmental prospective and profiling.

In water environmental management, the communication gap (CG) between water authorities and public causes difficult chronic management problem in water-environmental monitoring and assessment [5]. The potential solution is to prepare useful information, where our multi-parameter convenient approach will contribute to give new approach to solve the CG by rapid delivery of data, low-cost, and high capacity to acquire large number of observations of integrated data.

5. CONCLUSION

Ion Chromatography and Flow Injection Analysis integration was performed, which was satisfactory to analyze SO_4^{2-}, Cl^-, NO_3^-, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, NO_2^-, and PO_4^{3-} in $\mu M/L$ level, and EC in s 0.03 $\mu S/cm$ by only one equipment within 2*mL* onsite filtered sample. The analysis can be extended

to COD, TP, and TN. A convenient water quality prospecting was available for strategic environmental monitoring due to rapid delivered, low-cost, and integrated data.

6. ACKNOWLEDGEMENTS

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