Talanta 81 (2010) 1040–1044

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A low-cost method for determination of calcium carbonate in cement by membraneless vaporization with capacitively coupled contactless conductivity detection

Kamonthip Sereenonchai[a,b], Saowapak Teerasong[a,c], Sumonmarn Chan-Eam[a,b], Phoonthawee Saetear[a,b], Nathawut Choengchan[a,d], Kanchana Uraisin[a,b], Natchanon Amornthammarong[a,e], Shoji Motomizu[f], Duangjai Nacapricha[a,b,*]

[a] Flow Innovation-Research for Science and Technology (FIRST) Laboratories, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400 Thailand
[b] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400 Thailand
[c] Institute for Innovative Learning, Mahidol University, Phuttamonthon 4 Road, Nakhon Pathom 73170, Thailand
[d] Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Chalong Krung Road, Bangkok 10520 Thailand
[e] National Oceanic & Atmostpheric Administration (NOAA), Ocean Chemistry Division/AOML, Miami, FL 33149, USA
[f] Department of Chemistry, Faculty of Science, Okayama University, Okayama 800-8530, Japan

ARTICLE INFO

Article history:
Received 30 October 2009
Received in revised form 25 January 2010
Accepted 27 January 2010
Available online 4 February 2010

Keywords:
Carbonate analysis
Contactless conductivity
Membraneless vaporization
Carbon dioxide
Cement

ABSTRACT

This work presents a flow analysis method for direct quantitation of calcium carbonate in cement without pretreatment of the sample. The method is based on online vaporization of CO_2 gas following acidification of the sample inside a small chamber that has a flow of acceptor solution passing around it. Solubilization of the CO_2 gas into the acceptor stream changes the conductivity of the acceptor solution causing an increase of signal at the capacitively coupled contactless conductivity detection (C^4D) placed at the outlet of the vaporization chamber. This chamber is an adaption from previous work reported on 'membraneless vaporization' (MBL-VP).

The method can be used in the quality control of production of mixed cement. These cement materials usually have calcium carbonate contents at high concentration range (e.g., 33–99% (w/w) $CaCO_3$). Analysis of samples by this method is direct and convenient as it requires no sample pretreatment. The method is low-cost with satisfactory accuracy and acceptable precision.

1. Introduction

Calcium carbonate plays an important role in the property of cement and cement products. The content of calcium carbonate required in the calcareous raw materials such as limestone and chalk must be at least 80% (w/w) [1]. After calcination to produce cement clinker, the content of calcium carbonate must not be greater than 3% (w/w) [1]. However, in the production of mixed cement, Portland cement (finely ground mixture of the clinker and 5% (w/w) of gypsum) is mixed with calcium carbonate to obtain certain specified properties and with controlled contents of calcium carbonate (usually from 30 to 50% (w/w)).

As content of calcium carbonate plays a crucial role in cement production and in the property of mixed cement, there is a need to monitor calcium carbonate contents at several steps during production. In the literature, there are many methods reported for analysis of carbonate and carbon dioxide but mostly for water or liquid mixtures [2–6]. There are some methods available for determination of calcium carbonate in soil [7–11]. For cement, there was a FT-IR spectroscopy, based on making pellets of KBr containing cement samples, presented in 2001 [12]. However, this method is tedious as the sample must be carefully ground to a certain micron size to avoid light scattering [13]. As far as the authors' knowledge, methods available in the literature for direct detection of calcium carbonate in cements are limited. There are more information in some websites of commercial instruments, known as 'carbon–sulfur analyzer', for direct and rapid analysis of carbon and sulfur [14–16]. The content of calcium carbonate can be obtained from the result of the carbon analysis. In principle, cement sample is heated with gaseous production of CO, CO_2 and SO_2, which can be detected by IR spectroscopy.

For aqueous samples, a popular method for analysis of carbonate has been a membrane-based technique often called 'gas-diffusion' (GD) [2] or 'gas-permeation' [3]. Anionic species such as carbonate

* Corresponding author at: Flow Innovation-Research for Science and Technology (FIRST) Laboratories, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand. Tel.: +66 2 201 5127; fax: +66 2 201 5127.
E-mail address: scdnc@mahidol.ac.th (D. Nacapricha).

0039-9140/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2010.01.057

and its related form are acidified on-line to give gaseous CO_2, which then diffuses across a hydrophobic semi-permeable membrane into an acceptor solution. Detection of CO_2 in the acceptor stream can be carried out using various techniques, such as photometric detection of acid-base indicators [2–4], potentiometric detection using a tungsten oxide electrode [17], thermometric detection [18], piezoelectric-impedance detection [19], acoustic wave-impedance detection [20], traditional conductometric detection [3], and contactless conductivity detection [5,6].

However, for solid samples, pervaporation is more suitable than gas-diffusion. Pervaporation (PV) is similar in its concept to GD but differs in the design of the sample chamber. PV chamber has an air gap between the donor solution and the membrane [21]. This narrow air gap prevents direct contact between sample and the membrane and thus prolongs the life-time of the membrane. Selective permeation of CO_2 vapor across the non-wetting membrane to the acceptor can still occur with this arrangement. As with GD technique, non-specific detection like conductivity is applicable with the PV technique [7].

In the recent years, we have been focusing on the design of some membraneless (MBL) devices, which allows diffusion or vaporization of the gas from a donor to an acceptor stream, where it can be detected by photometry [22–24]. The concept of membraneless vaporization (MBL-VP) is similar to the GD and PV techniques, and is based on conversion of the analyte into a gas. In this technique, the configuration of the vaporization section (donor) and the acceptor flow is side by side in a closed chamber. In this way, the air space inside the chamber becomes a virtual membrane. For MBL-VP technique, it is not necessary to use a hydrophobic membrane like in GD and PV technique. The membraneless design has been shown to provide a better mass transport of the gas than the conventional GD technique, as reported for ethanol analysis [22]. In the latest design, a MBL-VP unit was developed for accommodating direct analysis of solid calcium carbonate with pH colorimetric detection using the cresol red [24].

This present work describes a low-cost system that utilizes the membraneless vaporization (MBL-VP) technique together with a contactless conductivity detection for determination of calcium carbonate in cement products by flow analysis. Analyses require no sample pretreatment. The concept of selective vaporization and the transfer of CO_2 gas into the acceptor stream is employed. Detection of the acceptor is based on changes in its conductivity, which is related to the amount of absorbed CO_2. We employ a 'capacitively coupled contactless conductivity detection' or C^4D as detector. This is the first time that C^4D has been used with the membraneless technique. In the past, C^4D has been used mostly in separation techniques like capillary electrophoresis (CE) and high performance liquid chromatography (HPLC) [25]. Although a group of researchers has presented the use of a similar detector to C^4D with gas diffusion technique for analysis of carbonate in model water sample, the flow cell was not easy to construct [5,6]. Here we employ the simple axial design of C^4D, commonly used for CE, for detecting the change in the conductivity of the acceptor stream from the MBL-VP unit. The C^4D system is applicable for a wide detection range and is suitable for the monitoring of calcium carbonate content in cement samples.

2. Experimental

2.1. Standards and reagents

All chemicals used were of analytical reagent grade. Deionized-distilled water was employed for preparations of standard and reagent solutions.

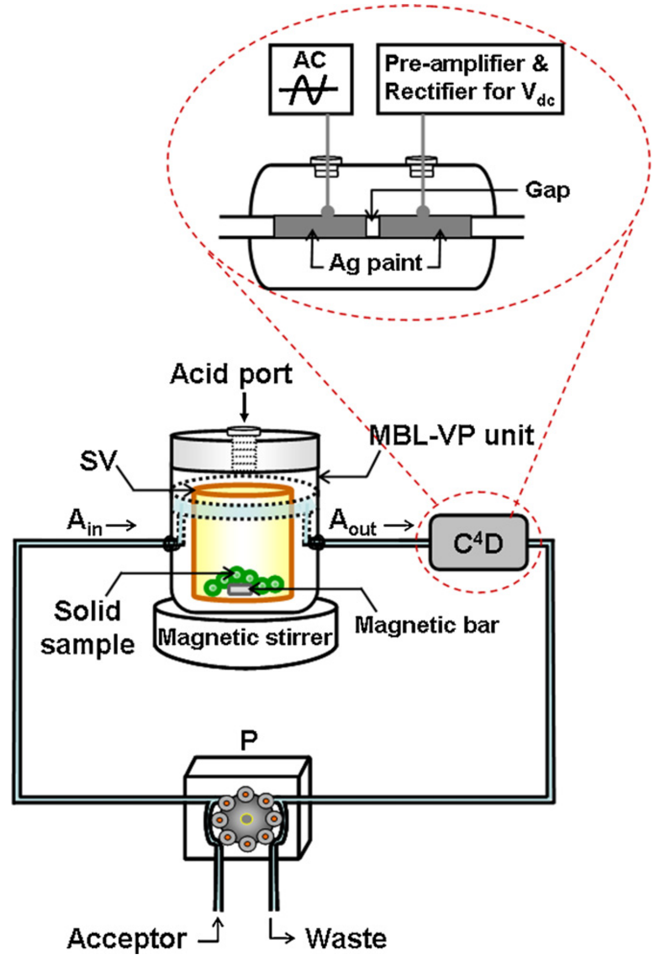

Fig. 1. The MBL-VP-C^4D manifold for direct analysis of calcium carbonate in cements. MBL-VP unit: membraneless vaporization unit, SV: sample vial, A_{in}: acceptor in, A_{out}: acceptor out, P: peristaltic pump. *Note*: the acceptor was 1 mM Tris and 1 μM KCl.

In optimization, it is more convenient to use solutions of sodium hydrogen carbonate as representative of calcium carbonate. For the optimization studies, the stock solution was prepared by dissolving 3.4 g (accurate weight) of sodium hydrogen carbonate (Merck, Germany) in water and made up to 50.00 ml. Further dilutions were made from the standard stock solution using water. For calibration and analysis of cement samples, calcium carbonate powder Carlo-Erba, Italy) was used as the standard.

The acceptor stream (Fig. 1) was prepared by mixing 10.0 ml of 100 mM Tris(hydroxymethylamino) methane (Merck, Germany) with 20.0 ml of 50 μM KCl with subsequent dilution to 1000 ml with water.

2.2. Manifold set up

Fig. 1 is a schematic diagram of the flow manifold for determination of calcium carbonate content, with the MBL-VP unit for formation and separation of the CO_2 gas and the C^4D for detection. Similar to that described in the previous work for the calcium supplement tablets [24], cement samples were accurately weighed (30 mg) into vials. The vial, followed by a clean magnetic bar, was placed inside the MBL-VP unit for subsequent vaporization and detection of CO_2. The flow system was operated using 'continuous flow mode' accordingly to the procedure shown in Table 1. PTFE tubes (0.75 mm i.d.) were used for all the flow lines, except in the detection cell of C^4D. An Ismatec peristaltic pump (model IS7610,

Table 1
Operating procedure of the MBL-VP-C4D flow system (Fig. 1) for analysis of calcium carbonate.

Step	Duration time (s)	Operational step	Pump	Lid
A	0–4	Place the vial containing solid standard/sample into the MBL-VP unit	On	Open
B	5–10	Close lid and prepare for acid injection	On	Close
C	11–90	Inject acid into sample vial	On	Close
D	91–240	Open MBL-VP lid to release residual $CO_{2(g)}$	On	Open

Switzerland) was used for the liquid flow. A magnetic stirrer (Hytrel HTR 8068, Germany) was employed continuously and set at a fixed speed for reproducible mixing of carbonate with hydrocholoric acid for both standards and samples.

2.3. Detection by C4D

The flow cell of C4D is schematically shown in the dotted area of Fig. 1. The cell was made from PEEK tubing (1 mm i.d. and 1.6 mm o.d.). The total length of the tubing was 150 mm. However the length of both electrodes were 10 mm each and were made by painting the PEEK tube with silver paint varnish [26], and with a gap of (0.2 ± 0.05 mm), separating the electrode. An AC signal was introduced to one of the metallic painted electrode from a function generator (GW Instek, SFG-2104, Taiwan). The AC-current from the second electrode was amplified, rectified and digitized, as reported by J.A.F. da Silva and C.L. do Lago [26], but using an in-house detection unit, coupled to a personal computer.

3. Results and discussion

3.1. Configuration of the C4D cell

In 2005, the group of F. Opekar reported an approach of making a contactless conductivity detection cell [5,6], called 'thinly insulated wire cell' (TIWC). They coupled this cell to gas-diffusion for determination of total inorganic carbon in liquid samples by flow injection analysis. This TIWC is based on the same concept of C4D and was made by inserting thin insulated wires through four punctured-positions of a PTFE tubing with 0.25 mm i.d. and 1.56 mm o.d. The insulation of the wire isolates and prevents direct contact between the metal wire and the solution. This TIWC design gave a significantly higher sensitivity than the axial configuration. However, the TIWC design has high risk of leakage and it is not simple to make.

In this work, we selected to use the design of axial tubular electrodes for the C4D flow cell. In order to enhance sensitivity, larger tubing with 1 mm i.d., instead of the capillary (~50–75 μm i.d.), was chosen. For the MBL-VP technique, there is no chromatographic resolution to be concerned with. Thus, the i.d. of the C4D cell may be increased even wider than 1 mm if desirable. PEEK or PTFE material may be used. A PEEK tubing was selected for making the cell because painting of the silver varnish on PEEK material was more convenient than the PTFE.

3.2. Optimization of the C4D

Prior coupling the C4D with the MBL-VP unit, the detection condition was optimized. A single line flow injection system (not shown) was assembled for this work. The buffer (mixture of 1 mM Tris and 1 μM KCl) was pumped through the tubular C4D cell. Repetitive injections (2.5 ml) of 0.02 mM sodium hydrogen carbonate solution were made at the input voltage

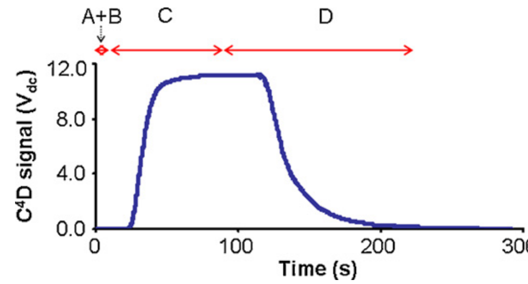

Fig. 2. Example of signal profiles obtained from the developed MBL-VP-C4D systems for analysis of solid sample: profile of 0.24 mmol CO_3^{2-} with acceptor flow rate at 2.4 ml min^{-1}. *Note*: the capital letters refer to the operating procedure in Table 1.

(V_{p-p}) of 20 V. The signal increased as the AC frequency was increased from 10 to 25 kHz. Beyond 25 kHz (50–100 kHz), the signal decreased. Therefore, we selected 25 kHz at 20 V_{p-p} as the input signal.

The length of silver bands painted on PEEK tube of 10 or 20 mm did not give significant difference in the sensitivity, and 10 mm was chosen as the electrode length. In order to maintain the same sensitivity, the gap between the two silver bands was always fixed at 0.20 ± 0.02 mm for every C4D cell constructed.

3.3. Signal profile

As shown in Fig. 2, the signal is not a symmetrical peak. With the employed operating procedure (Table 1), which is a continuous flow mode, the signal typically reaches a plateau during the acid injection step C. The signal then drops to baseline as the lid was opened after 91 s in step D. In this work, we used the height of the signal taken at 80 s for the calibration.

3.4. Final operating condition

Optimization can be divided into two parts, that involving C4D detection and the other including the flow system. Optimization for the highest signal was described in Section 3.2. Table 2a lists the C4D parameters, which are employed for the analysis of cements. The various parameters and the final selected values, for the flow system, are given in Table 2b.

3.4.1. Sample size

Cement samples usually contain relatively high content of calcium carbonate (from 25 to 100%, w/w). Due to the high sensitivity

Table 2
Recommended condition of the MBL-VP-C4D flow system for determination of calcium carbonate.

Parameters	Studied	Selected
C4D sensor		
1. Applied frequency (kHz)	10–100	25
2. Applied voltage (V_{p-p})	10–20	20
3. The tubular cell		
3.1 inner diameter (PEEK) (mm)	0.25–1.00	1.00
3.2 length of silver paint (mm)	10–20	10
MBL-VP and the flow condition		
1. Sample size per analysis	5, 10, 20, 30 mg	30 mg
2. Acceptor stream		
2.1 components	Water, *x* Tris + *y* KCl	1 mM Tris + 1 μM KCl
2.2 flow rate (ml min^{-1})	0.5–3.0	2.5
3. Volume of 3 M HCl per analysis (ml)	0.5–1.0	1.0

x: 0.1, 0.5, 1 and 3 mM.
y: 0, 0.1, 1 and 5 μM.

Table 3
Analytical features of the MBL-VP-C^4D flow system for determination of calcium carbonate.

Feature	Value
1. Linear working range	0.04–0.24 mmol $CaCO_3$ (4–24 mg $CaCO_{3(s)}$)
2. Equation; r^2	$V_{dc} = (29.57 \pm 2.90)$ (mmol $CaCO_3$) + (3.168 ± 0.438); $r^2 = 0.991$
3. Throughput (samples h^{-1})	14
4. Precision (%RSD)	5.3 (20 mg $CaCO_3$, $n = 10$)
5. Detection limit (3S/N)	2.5 μmol $CaCO_3$ (0.25 mg $CaCO_{3(s)}$)
6. Direct analysis of sample as received?	Yes
7. Applicable with external calibration?	Yes (using $CaCO_3$ solution or $CaCO_3$ powder)
8. Sample preparation	- None (proximate analysis) - Oven dry (accurate analysis)

of our C^4D, an appropriate amount of solid sample must be selected in order not to exceed the linear working range of the system. For cement and related materials, we found that 10–30 mg is sufficient. Finally, 30 mg was chosen as the optimum sample weight (Table 2b). Each sample must be weighed using five-digit microbalance for ensuring the mass precision.

3.4.2. *Acceptor line*

3.4.2.1. Type of acceptor solution. We observed that plain water (deionized-distilled water, pH 6) may be used as the acceptor stream for the system in Fig. 1. Nevertheless, we still prefer to use a weakly buffered solution for absorbing the CO_2 vapor. In some work, reporting the trapping of CO_2 via membrane-gas diffusion [19,20], solution of Tris (10 mM) and KCl (0.5 or 1 mM) was reported as a suitable acceptor stream. However, these concentrations of Tris and KCl were not suitable for our C^4D system, due to the high conductivity. Therefore, the concentrations of Tris and KCl were reduced using 1 mM sodium hydrogen carbonate as the test sample. Fig. 3 shows that 1 mM Tris and 1 μM KCl gave the highest sample signal but with suitable baseline values. Thus a mixture of 1 mM Tris and 1 μM KCl were selected as the acceptor solution for both systems in Fig. 1.

3.4.2.2. Flow rate. In a flow system with incorporation of a gas-trapping device, flow rate of the acceptor stream is a key parameter that determines sensitivity of the system. Results showed that as the flow rate was increased from 0.5 to 3 ml/min, the signal decreased by 50%. As a compromise between sample throughput and the detection limit, the flow rate of acceptor stream was set at 2.5 ml/min for the system in Fig. 1 (Table 2b).

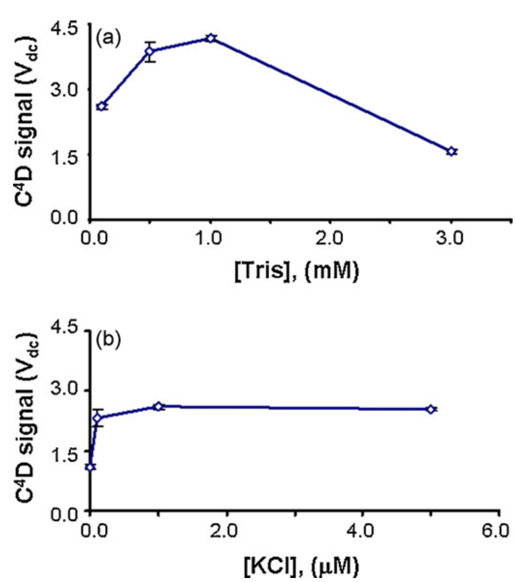

Fig. 3. Effect of concentrations of (a) Tris and (b) KCl in the acceptor solution on the signal. The experiments were carried out using repetitive injections of 1 mM sodium hydrogen carbonate.

3.4.3. *Donor*

In order to generate CO_2 gas stoichiometrically from cement sample, the acid was injected into the sample vial through the acid port situated on the lid of MBL-VP unit (Fig. 1). The results show that 1 ml of 3 M hydrochloric acid was excess enough for complete solubilization of the samples of cement and raw material.

3.5. *Analytical feature*

The final analytical features of the MBL-VP-C^4D system are summarized in Table 3. Linear calibration ($r^2 > 0.99$) was obtained from 4 to 24 mg $CaCO_{3(s)}$. The throughput of 14 sample h^{-1} is notable since off-line sample preparation is not needed. Vaporization of the analyte to form CO_2 vapor before detection allowed use of external calibration method, which is very convenient. With the external calibration, the recovery is from 85 to 103%. Our method is very precise with %RSD of 5.3.

3.6. *Application, validation and comparison to commercial instruments*

The flow system in Fig. 1 was applied to eight cement materials (Table 4). Sample numbers 1–4 are the raw materials. Sample numbers 5–8 are the commercial mixed cement products. The low values of SD in Table 4 show that the developed method is precise and suitable for using in the quality control of cement industry. We also employed a commercial 'carbon–sulfur analyzer' for comparison. By means of statistical paired t-test [27], the calcium carbonate contents, determined by the MBL-VP C^4D techniques, are not significantly different from contents given by the method of carbon–sulfur analyzer at 95% confidence ($t_{stat} = 0.764$, $t_{crit} = 2.447$). This shows that our developed methods are accurate and reliable. Our system is lower cost than the commercial carbon–sulfur analyzer instruments, which are based on temperature programmed combustion of the sample to generate CO_2 gas followed by infrared detection [14–16].

Table 4
Validation of our method by comparing the results with the carbon–sulfur analyzer.

Sample	% (w/w) $CaCO_3$ (mean ± SD, $n = 3$)	
	The proposed method	Carbon–sulfur analyzer
1. Limestone 1	89.02 ± 0.08	96.38 ± 0.48
2. Limestone 2	99.23 ± 1.95	99.62 ± 0.04
3. Chalk 1	93.05 ± 3.56	91.85 ± 0.63
4. Chalk 2	93.11 ± 2.43	93.47 ± 0.05
5. Mixed cement 1	33.49 ± 1.55	30.15 ± 0.03
6. Mixed cement 2	41.64 ± 2.47	46.88 ± 0.05
7. Mixed cement 3	44.42 ± 0.52	46.89 ± 0.67
8. Mixed cement 4	49.71 ± 1.82	47.00 ± 0.47

4. Conclusions

This work describes a new flow system consisting of a so-called 'membraneless vaporization' unit and a flow-through tubular cell based on the concept of capacitively coupled contactless conductivity detection or C^4D. This flow system is capable of measurements of calcium carbonate contents in cement samples. The method is direct and requires no pretreatment step. Sample is introduced directly into the system followed by acidification of the sample to generate vaporization of the CO_2 gas inside the membraneless vaporization unit. Subsequent solubilization of the CO_2 gas causes the conductivity of the acceptor stream to increase, resulting in the rise in the voltage signal at the C^4D detector. Utilizing vaporization with subsequent trapping of the CO_2 gas is not dependent on the form of the standard (solid or liquid). Therefore, this allows us to conveniently use external calibration method. The system and procedure have been successfully applied to commercial cement products.

The tubular flow cell of the detector is much simpler than the 'thinly insulated wire cell' [5,6], which was made by using a capillary tubing (0.25 mm i.d.) with four punctured holes. The flow cell used in our work employs a PEEK tube with no punctured holes and therefore there is no chance of liquid leakage to occur. The i.d. of the PEEK tubing is 1 mm, and will not produce any back pressure. Linear range of our C^4D detector covers the wide range of calcium carbonate contents found in the cement samples. In our previous study using dye indicator, the linear range of detection was more limited [24]. Thus, for analysis of calcium carbonate with vaporization of CO_2 with trapping of the gas in an acceptor solution, C^4D has been shown to be a detector of choice.

Acknowledgements

The authors would like to acknowledge the financial supports of the project from the Thailand Research Fund (TRF) (DN) and the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education). The TRF student scholarship through the Royal Golden Jubilee-Ph.D. program (KS) was gratefully acknowledged. The authors would like to thank Assoc. Prof. Prapin Wilairat for the editing.

References

[1] http://www.bgs.ac.uk/downloads/directDownload.cfm?id=1408&noexcl=true&t=Cement%20Raw%20Materials.
[2] S. Motomizu, K. Toei, T. Kuwaki, M. Oshima, Anal. Chem. 59 (1987) 2930.
[3] V. Kuban, P.K. Dasgupta, Talanta 40 (1993) 831.
[4] M. Oshima, Y. Wei, M. Yamamoto, H. Tanaka, T. Takanayagi, S. Motomizu, Anal. Sci. 17 (2001) 1285.
[5] Z. Hoherčáková, F. Opekar, Anal. Chim. Acta 551 (2005) 132.
[6] Z. Hoherčáková, F. Opekar, K. Štulík, Electroanalysis 17 (2005) 1924.
[7] M.Y. Kamogawa, A.R.A. Nogueira, M. Miyazawa, J. Artigas, J. Alonso, Anal. Chim. Acta 438 (2001) 273.
[8] F. Gaal, I. Szollosy, M. Arnold, F. Paulik, J. Thermal Anal. 42 (1994) 1007.
[9] B. Horvath, O. Opara-Nadi, F. Beese, Soil Sci. Soc. Am. J. 69 (2005) 1066.
[10] M. Tatzber, M. Stemmer, H. Spiegel, C. Katzlberger, G. Haberhauer, M.H. Gerzabek, Environ. Chem. Lett. 5 (2007) 9.
[11] F. Paulik, J. Paulik, M. Arnold, J. Thermal Anal. 29 (1984) 333.
[12] M.A. Legodi, D. de Waal, J.H. Potgieter, S.S. Potgieter, Miner. Eng. 14 (2001) 1107.
[13] N.V. Vagenas, A. Gatsouli, C.G. Kontoyannis, Talanta 59 (2003) 831.
[14] http://www.horiba.com/fileadmin/uploads/Scientific/Documents/Emission/EMIGA24.pdf.
[15] http://www.leco.com/products/organic/sc_632/sc_632.htm.
[16] http://www.behr-labor.com/pdf/CS50HT-e.pdf.
[17] L. Monser, N. Adhoum, S. Sadok, Talanta 62 (2004) 389.
[18] S.J. Liu, M. Tubino, Talanta 47 (1998) 711.
[19] X.L. Su, H.W. Tan, W.F. Li, W.Z. Wei, S.Z. Yao, Anal. Sci. 14 (1998) 533.
[20] X.L. Su, L.H. Nie, S.Z. Yao, Anal. Chim. Acta 349 (1997) 143.
[21] I.L. De Mattos, M.D. Luque de Castro, M. Valcárcel, Talanta 42 (1995) 755.
[22] N. Choengchan, T. Mantim, P. Wilairat, P.K. Dasgupta, S. Motomizu, D. Nacapricha, Anal. Chim. Acta 579 (2006) 33.
[23] S. Muncharoen, J. Sitanurak, W. Tiyapongpattana, N. Choengchan, N. Ratanawimarnwong, S. Motomizu, P. Wilairat, D. Nacapricha, Microchim. Acta 164 (2009) 203.
[24] K. Sereenonchai, P. Saetear, N. Amornthammarong, K. Uraisin, P. Wilairat, S. Motomizu, D. Nacapricha, Anal. Chim. Acta 597 (2007) 157.
[25] P. Kuban, P.C. Hauser, Electrophoresis 30 (2009) 176.
[26] J.A.F. da Silva, C.L. do Lago, Anal. Chem. 70 (1998) 4339.
[27] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, 4th ed., Pearson Education, Essex, 1993.