RESEARCH ARTICLES

SPECTROPHOTOMETRIC DETERMINATION OF SILICON IN KAOLINS BY FLOW INJECTION ANALYSIS

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ABSTRACT

A flow injection analysis procedure is described by which dissolved silicon can be determined in complex aqueous media such as soil extracts. The spectrophotometric determination is based on yellow silicomolybdate. A soil sample solution is prepared by fusion with sodium hydroxide and subsequent dissolution of the cake in 6 M hydrochloric acid. The flow system permits high throughput of 120 samples h^{-1} without any carryover. The procedure has been applied to kaolins from various parts of Thailand and gave satisfactory agreement with the recommended method.

INTRODUCTION

The increasing demand of rapid methods for continuous determinations of organic and inorganic compounds, which are suitable for automated analysis of large numbers of samples has led to the development of continuous flow analysis (CFA). Techniques in CFA can be divided into two categories : segmented flow analysis (SFA) and flow injection analysis (FIA).

Since the publication of Skeggs classic work[1] on SFA, it has been generally understood that air segmentation of the flowing stream and steady state operation are essential for analysis by continuous flow methods. However, in 1975, Ruzicka and Hansen[2] have proposed a new concept of CFA, termed flow injection analysis. They consider that the segmented flow systems complex in terms of operation and equipment due to the compressibility of air which causes the stream to pulsate rather than flow regularly and limits possibilities to miniaturize the system.

FIA is based on injecting the sample directly into a non-segmented carrier stream and the resulting analytical readout is in the form of transient peak. FIA has been widely used for automatic continuous analysis in agricultural, clinical, pharmaceutical and environmental

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chemistry, owing to the high throughput and cost effectiveness.[3] We have been attempting to apply FIA to the determination of aluminium in kaolins[4]. The work has now been extended to silicon which is the other major element in kaolin besides aluminium. Grade of kaolin is determined by the aluminium content while the amount of silicon would indicate its industrial applications.

There are many papers describing the spectrophotometric determination of silicon, but almost all are variations of two basic methods, i.e. the yellow silicomolybdate and the molybdenum blue methods. We decided to employ the yellow method for an flow injection spectrophotometric analysis of silicon to prove that the proposed NaOH digestion procedure[4] enables adequate decomposition of the inorganic matrix and hence permits accurate determination of various elements in kaolin.

MATERIALS AND METHODS
Chemicals

All reagents used were of analytical-reagent grade. Ammonium molybdate used was from Fluka and other chemicals used were from BDH.

Standards

Silicon stock solution (500 μg ml^{-1}) was prepared as follows. 5.0 g of sodium hydroxide were fused in a zirconium crucible and allowed to cool. 0.5358 g of quartz powder (99.8% silica) were added into the crucible and then fused again for 3-5 min. The cool melt was extracted with triply distilled water and diluted to 500 ml.

To prepare ammonium molybdate solution, 3.75 g of ammonium molybdate were dissolved in 5 ml of water. 2.50 ml of concentrated sulphuric acid were added to the solution and made up to a volume of 250 ml. The solution was left in a plastic bottle for 24 h before use.

Synthetic kaolin sample was prepared as described in the previous report.[4]

Instruments and Methods

Instruments and methods for both FIA and the recommended classical method[5] were similar to the previous report[4].

Pre-treatment of sample solution for FIA

An aliquot containing about 2-7 mg of silicon was made alkaline with sodium hydroxide pellet in a plastic beaker and then warmed on a water bath for 5 min. The precipitate was filtered off and washed with hot water. The filtrate was then acidified with 1:1 sulphuric acid and diluted to 50 ml.

RESULTS AND DISCUSSION
Colour development

The spectrophotometric determination of silicon was based on the formation of yellow silicomolybdate complex. Fig. 1 shows the absorption spectra of ammonium molybdate measured
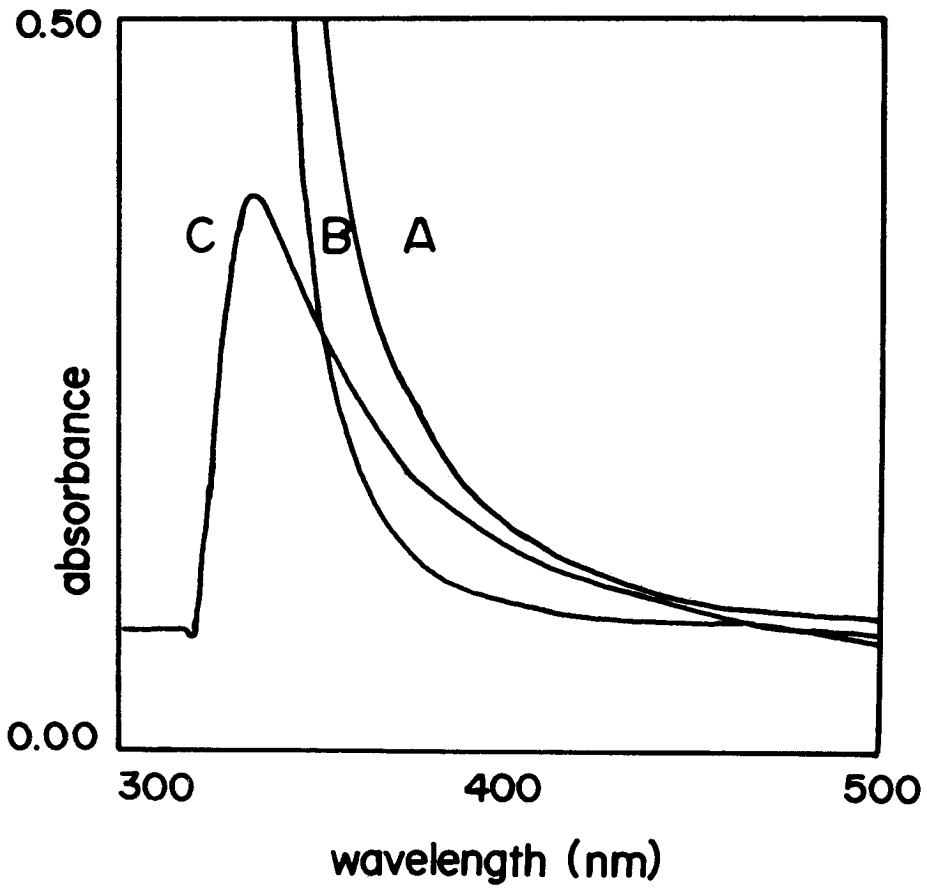
Fig. 1. Absorption spectra of molybdic acid its silicon complex : A, ammonium molybdate in sulphuric acid measured against water; B and C, silicon in the ammonium molybdate solution measured against water and the blank, respectively.

against water and of silicomolybdate complex measured against water and the blank solution. The maximum absorbance of silicomolybdate measured against the blank was at 340 nm. However, the absorbance of the reagent itself was also high at this wavelength and therefore it was difficult to adjust the background to zero on the single beam spectrophotometer. Thus, the choice of the fixed wavelength for the FIA measurement was 400 nm in order to obtain the highest sensitivity (signal : background ratio).

The rate of colour development of silicomolybdate at 25°C is shown in Fig. 2A. It took nearly 8 min for the formation of silicomolybdate to reach 95% complete reaction. When the reagent was prepared and stored for at least 24 h, the sensitivity was doubly increased. However, the colour development proceded at the similar rate (Fig. 2B). A further increase in sensitivity together with rate of reaction can be achieved by warming the solution to 50°C (Fig. 2C).

Optimization of flow injection measurements

A response of the detector employed in flow injection analysis depends on the hydrodynamic conditions and the kinetics of the chemical process involved in the detection mechanism. In this study some experimetal parameters such as sample injection volume, flow rate, and length of the analytical line, were examined. The effect of the sample volume was investigated by injecting various sample volumes of 30 ppm standard silicon solution into the reagent stream at the flow rate of 5.0 ml min^{-1}. A straight line was obtained when the peak height was plotted as a function of sample injection volume (Fig. 3). An increase in injection volume from 25 to 200 μl resulted in a signal increase of 680%. However, this was accompanied by a decrease in sampling rate from 240 to 156 samples h^{-1}.

Fig. 4 shows flow injection peaks obtained at various flow rates for 100 μl injection of 30 ppm silicon solution. An increase in peak height was observed when the flow rate was reduced from 5.0 to 1.0 ml min^{-1}. These results indicated that chemical kinetics dominated the flow injection response over the whole range of flow rate examined. A decrease in peak height occured at flow rates below 1.0 ml min^{-1} where the physical dispersion became dominant. An increase in peak width and a corresponding decrease in the maximum sampling rate were also found when the flow rate was reduced (Table 1).

When the length of the analytical line was changed within the range 50-200 cm, it was found that the recorded signal was slightly decreased with increasing tube length as shown in Fig. 5. The effect of dispersion on peak width can also be seen on Fig. 5. The effect of dispersion on peak width can also be seen on Fig. 5 which shows that the peak becomes wider when the tube length is increased.

Effect of sampling rate on reproducibility and carryover

Peak height reproducibility depends on several experimental factors such as stability of flow rate, reproducibility of injection volume, and sampling rate. The effect of sampling rate on peak height reproducibility (relative standard deviation, RSD) was examined for 10 replicate injections of 30 ppm silicon at various sampling rates in the range 60-180 samples
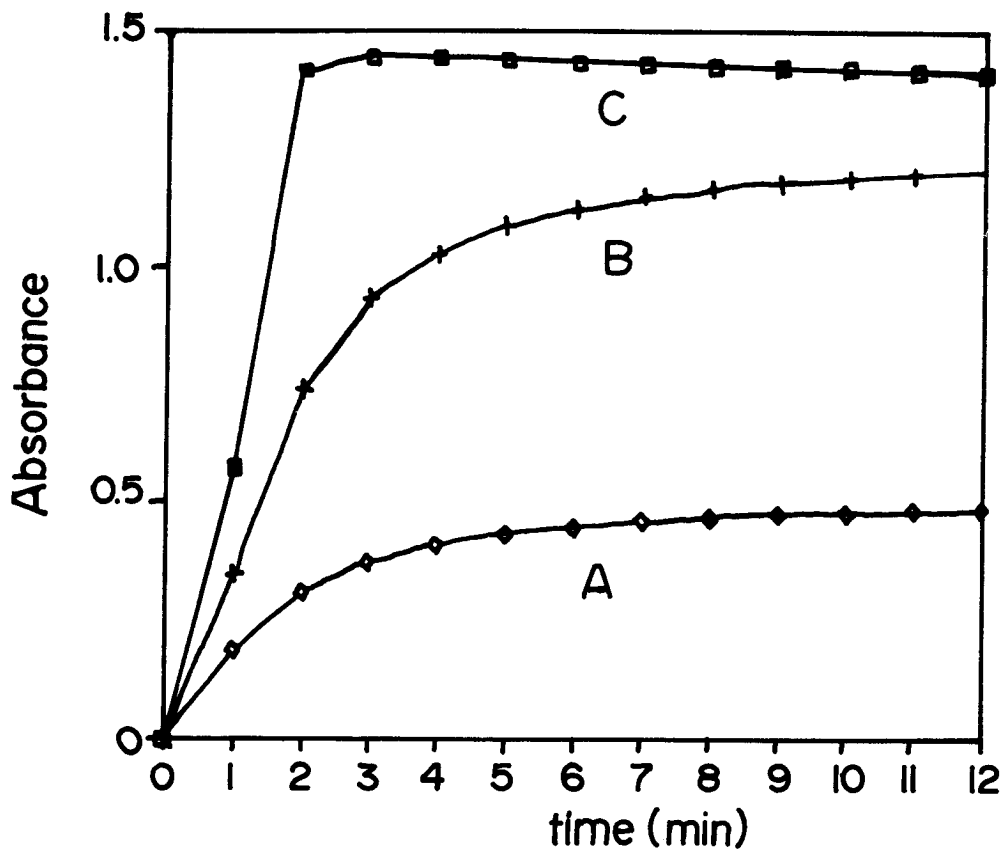
Fig. 2. Colour development of yellow silicomolybdate as a function of time : A, freshly prepared reagent; B, reagent prepared for at least 24 h before use; and C, freshly prepared reagent at 50°C.
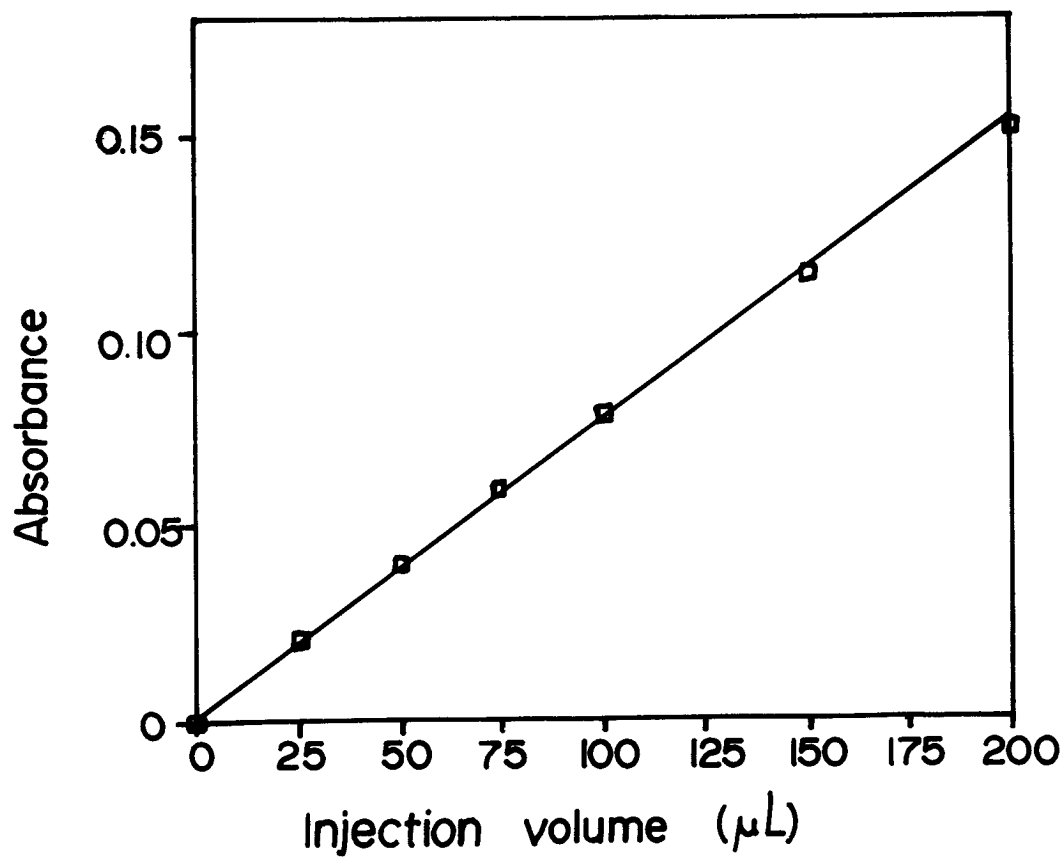
Fig. 3. Effect of sample injection volume on peak heights of 30 ppm silicon at a flow rate of 5.0 ml min^{-1}.
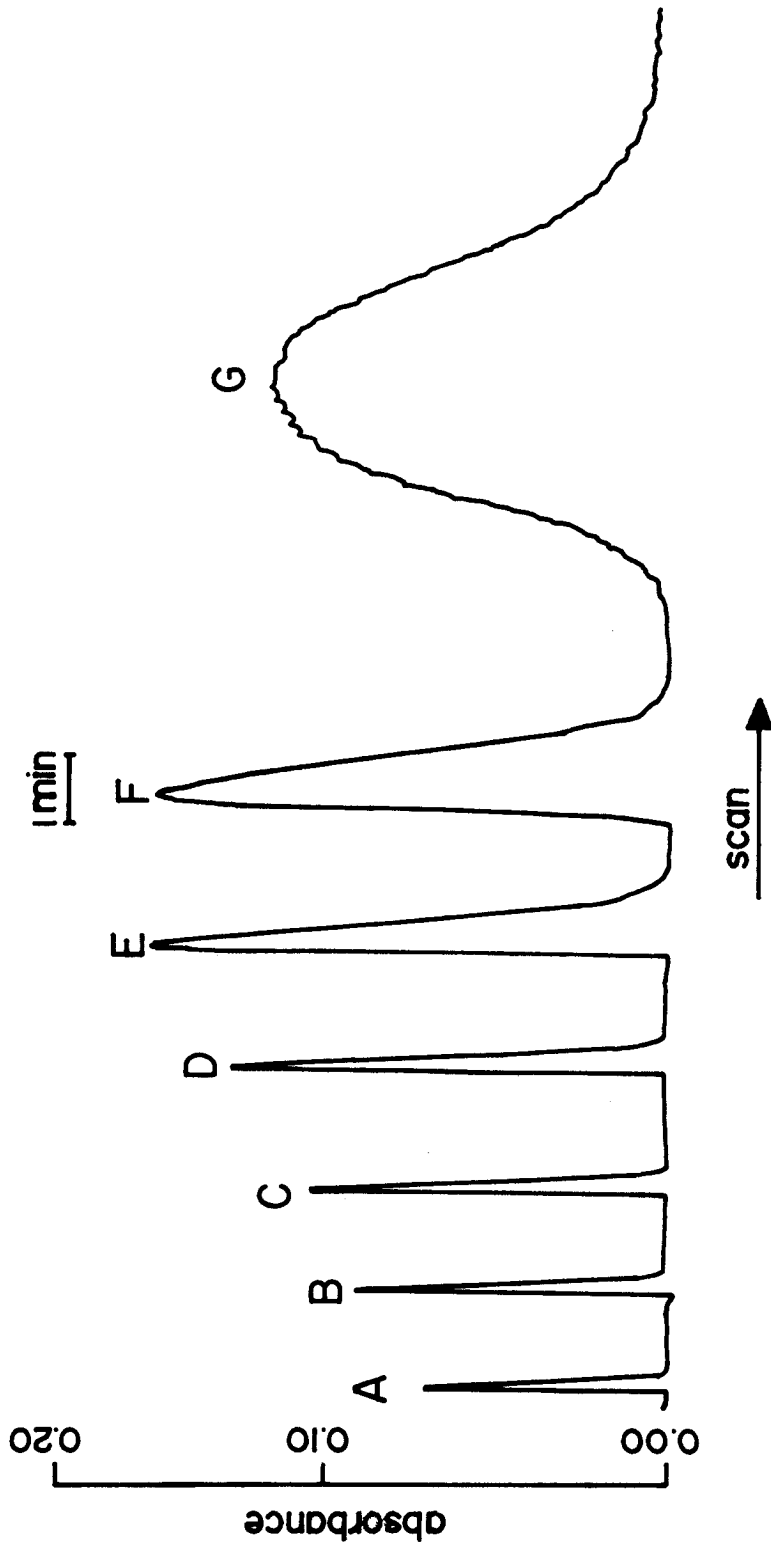
Fig. 4. Effect of flow rate on response peaks : A, 5.0; B, 4.0; C, 3.0; D, 2.0; E, 1.0; F, 0.5; and C, 0.1 ml min^{-1}.

TABLE 1. Effect of flow rate on sample peaks

Flow rate ($ml\ min^{-1}$)	Peak height (absorbance)	Peak width (sec)	Sampling rate (samples h^{-1})
5.0	0.075	18	200
4.0	0.101	21	171
3.0	0.116	24	150
2.0	0.148	36	100
1.0	0.179	72	50
0.5	0.170	132	27
0.1	0.132	462	8

TABLE 2. Effect of sampling rate on reproducibility and carryover

Sampling rate (samples h^{-1})	RSD[*] (%)	Carryover (%)
60	0.96	0.00
90	1.14	0.00
120	1.95	0.00
180	2.51	2.40

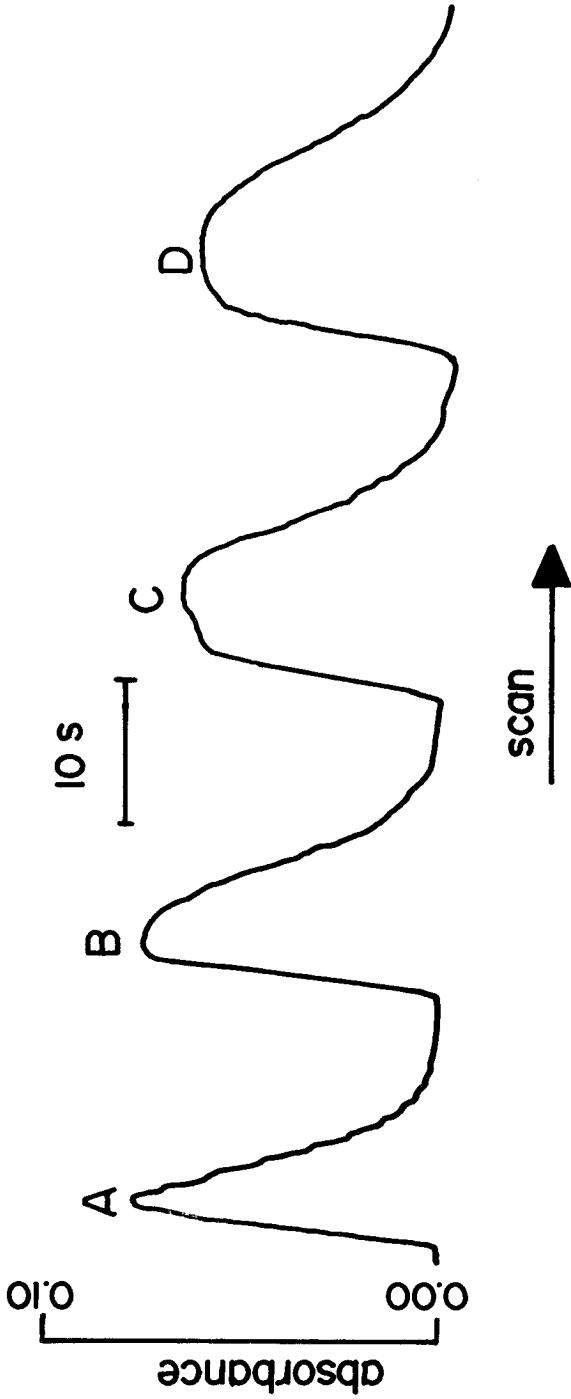[*]Relative standard deviation for ten replicates of silicon sample

Fig. 5. Effect of tube length on response peaks : A, 50; B, 100; C, 150; and D, 200 cm.

h^{-1}. The results shown in Table 2 demonstrated that the reproducibility was decreased with increasing sampling rate. Injecting sequential samples of 5, 30, and 5 ppm of silicon at sampling rates up to 120 samples h^{-1} gave no carryover as shown in Table 2.

Interferences

Interference study similar to the previous report[4] for the determination of aluminium in kaolins was investigated by using a standard solution containing 100 ppm silicon. Barium, calcium, cobalt, copper, lithium, magnesium, potassium, zinc and nitrate did not interfere even at the concentration as high as 200 ppm. Aluminium and iron at concentrations greater than 150 ppm and 80 ppm, respectively, gave positive interferences which could be diminished by precipitating as the metal hydroxide and filtering off during the pretreatment process. However, amounts of these ions in kaolin are less than that of silicon, especially iron of which the ratio 50:1 (silicon : iron) is normally found. Therefore these ions have no effect on the silicon determination. Phosphate (30 ppm) and manganese (25 ppm) gave also positive interferences. Oxalic acid, citric acid, and tartaric acid which were reported as a masking agent for phosphate ion[6] were found to be inadequate to suppress this interference in the flow system. These acids can decompose the phosphomolybdic acid and therefore can protect the effect of phosphate in batch analysis but not in the flow analysis due to limitation in time. For the soil analysis, amount of phosphate is reduced in sample preparation step; the sample is fused with sodium hydroxide and then dissoved in 1:1 hydrochloric acid, precipitation of zirconium phosphate is formed and filtered off. However, the interference of phosphate or manganese is not considered serious, as such phosphate to silicon or manganese to silicon ratios are never encountered in kaolins.

Sensitivity and detection limit

Fig. 6 shows the effect of reagent concentration on the calibration curves of silicon. The sensivity increased with an increase in the concentration of ammonium molybdate. A decrease in the sensitivity occurs at concentrations above 15.0 mg ml^{-1}; this concentration was considered to be the optimum. A linear working range was obtained for injections of 0 to 200 ppm with the correlation coefficient of 0.999. The detection limit was 1.0 ppm for silicon.

Determination of silicon in kaolins

Table 3 shows accuracy, precision and percentage recovery of the FIA method for the determination of silicon in the synthetic kaolin compared with those of the classical method. The results illustrated that the FIA method was more accurate and precise. The analytical feasibilities of the developed method were then tested on the determination of silicon in kaolins from various parts of Thailand. The results summarized in Table 4 demonstrates good agreement between both methods; however, the FIA method still shows better precision.
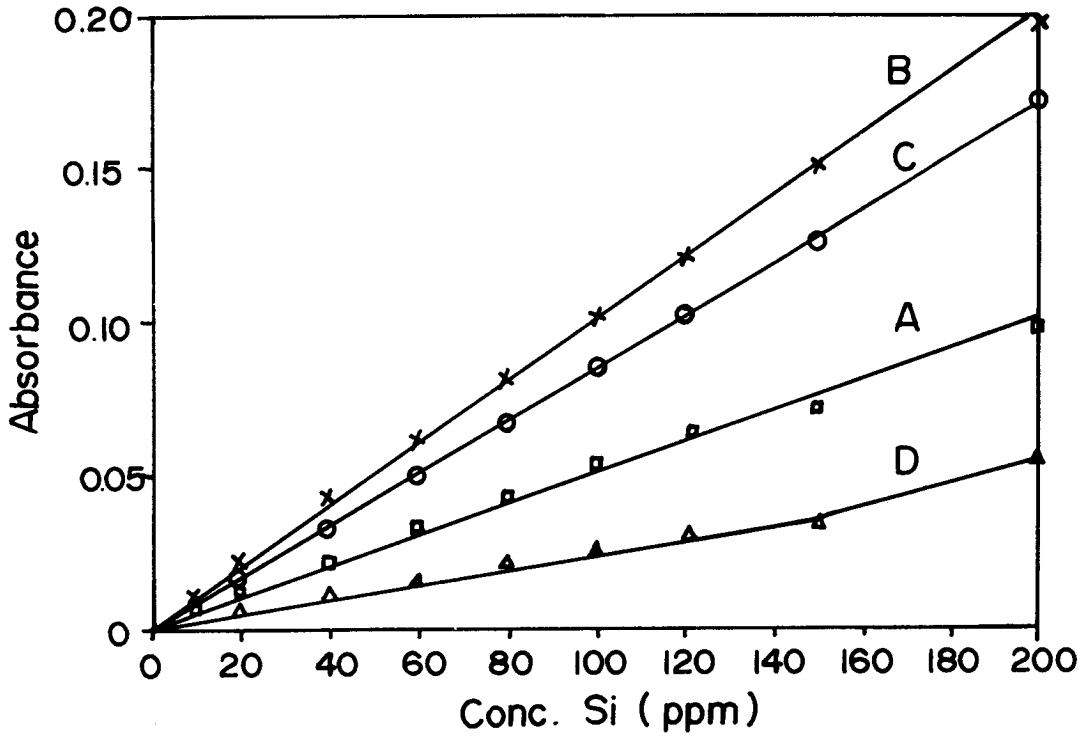
Fig. 6. Effect of reagent concentration on sensitivity of silicon determination : A, 7.5; B, 15.0; C, 22.5; and D, 30.0 mg ml^{-1} ammonium molybdate in 1% sulphuric acid, for a 75 μl injection at a flow rate of 5.0 ml min^{-1}.

TABLE 3. Determination of silicon in the synthetic sample (50.0% SiO_2)

Method	SiO_2 (% m/m)	Error (%)	RSD[*] (%)	Recovery (%)
FIA	49.82	0.36	1.02	99.64
Classical	48.74	2.52	1.92	97.48

[*]Relative standard deviation for ten extracts

TABLE 4. Determination of silicon in kaolins from various parts of Thailand.

Sample code[*]	FIA		Classical analysis	
	SiO_2 (% m/m)	RSD[**] (%)	SiO_2 (% m/m)	RSD[**] (%)
K–VP	47.21	1.02	46.03	1.34
K–JD	44.01	0.98	43.19	1.45
K–KM	48.41	1.14	47.63	1.99
K–PK	44.35	0.95	43.95	1.81

[*] K–VP : kaolin from Vaieng pa-pao district, Chiangrai

[*] K–JD : kaolin from Su-ngai padi district, Narathiwat

[*] K–KM : kaolin from Tungkha district, Ranong

[*] K–PK : kaolin from Khokmailai village, Prachinburi

[**]Relative standard deviation for ten soil extracts

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บทคัดย่อ

วิธีการวิเคราะห์แบบโฟลอินเจคชันสามารถตรวจหาซิลิคอนได้ในตัวกลางเชิงซ้อนแบบเอเควียส เช่น ส่วนสกัดจากดิน การตรวจหาด้วยวิธีสเปกโตรโฟโตเมตรีนี้ทำได้จากซิลิโคโมลิบเดทซึ่งมีสีเหลือง สารละลายจากดินตัวอย่างเตรียมโดยการหลอมกับโซเดียมไฮดรอกไซด์แล้วละลายในกรดไฮโดรคลอริก 6 โมลาร์ ระบบการไหลนี้สามารถทำให้วิเคราะห์ได้ถึง 120 ตัวอย่างต่อชั่วโมงโดยไม่มีแครรีโอเวอร์ ได้นำวิธีการนี้ไปประยุกต์ใช้วิเคราะห์ดินขาวจากแหล่งต่าง ๆ ในประเทศไทยและให้ผลสอดคล้องเป็นที่น่าพอใจกับวิธีที่ยอมรับ