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SEQUENTIAL INJECTION ANALYSIS: A POWERFUL TOOL

FOR ROUTINE SOIL AND PLANT LABORATORIES

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Abstract

Sequential injection analysis (SIA) present attractive characteristics for analyses in large scale. In SIA the analytical determination can be performed automatically reducing the number of steps usually involved in a chemical analysis. In order to demonstrate the advantages found in the implementation of a SIA procedure in a laboratory dedicated to routine analyze, the determination of volatile nitrogen in silage and soil samples has been performed. The nitrogen content was determined after NH_3 on-line separation in alkaline conditions by using a gaseous diffusion or a pervaporation unit for liquid-liquid separation. An ammonium tubular selective electrode detector was used for determinations.

Keywords: Large scale analyses, automation of analytical procedures.

Introduction

Quality control and characterization of agronomic materials are assessed determining different parameters which usually require several and many times tedious steps in the chemical analysis. Therefore, due to increase in the number of samples and the need of fast and reliable techniques, the automation of many analytical procedures has recently given

attention. Among the alternatives available to accomplish this purpose, flow methods have been proved to be suitable due to low sample and reagent consumption, high sample throughput and feasibility of their implementation. Proposed in 1990 (Ruzicka and Hansen), the sequential injection analysis is based on the sequential aspiration of the sample and reagent(s) aliquots by using a multiport valve and a liquid propulsion unit, both interfaced to a computer. Its has been efficiently applied in process control and/or in the developed of analytical procedures.

Material and Methods

The sequential injection systems, schematically described in Figure 1a and 1b, were constructed using two peristaltic pumps with variable rotation (Ismatec, Switzerland) and a six-way electrically actuated solenoid valve (NResearch, USA), both interfaced to a computer through a PCL 711-S interface board (American Advantech, USA). The manifolds were built up with 0.8 mm i.d. polyethylene tubing. Tygon tubing was used for pumping the solutions. Ammonium tubular selective electrode (Alegret et al. 1989) was used as detector in both proposed procedures. The gaseous diffusion unit consisted of two Perspex pieces, with semi-tubular grooves drilled in each piece, closed by screws. Between the entrance and exit sides of the grooves was inserted a PTFE membrane that promoted the NH_3 separation of the sample solution. The pervaporation unit consisted of two Perspex chambers, donor and acceptor chamber, aligned by screws . Between the acceptor and donor chamber there are spaces that avoid the direct contact between membrane and the sample solution. Both separator devices involve a gaseous diffusion through a hydrophobic membrane. However in the gaseous diffusion unit there is a direct contact between the donor solution and the membrane, while it is not observed in the pervaporation unit. In the system proposed to volatile nitrogen determination in silage (Fig. 1a), sample and alkaline reagent aliquots are sequentially aspirated, mixed and then carried to a holding coil (HC_1). After, the sample zone formed in

HC_1 was addressed to the gaseous diffusion unit, where the ammonia present in the donor chamber was diffused across the PTFE membrane. The diffused ammonia was collected by an acceptor stream that convert NH_3 to NH_4^+ and carried it toward the tubular ion selective and reference electrodes. In the system proposed to volatile nitrogen determination in soil, the solid sample is directly placed in the pervaporation donor chamber where alkaline solution is added. The ammonia formed diffused across the hydrofobic membrane and it was collected by an acceptor solution and directed to the potentiometric sensor.

Results and Discussion

The main experimental parameters of the systems studied were optimized and the analytical characteristics were evaluated in relation to the precision, accuracy, sample throughput and detection limit. For soil samples it were observed r.s.d < 3.0 % (n=10); detection limit of 0.28 mg l^{-1} N and 15 samples h^{-1} as analytical frequency with 2.0 g of soil sample consume. For silage, the r.s.d was < 2.0 % (n=10); the detection limit was 3.0 mg l^{-1} N and the analytical frequency presented 30 samples h^{-1} with 150 µl of silage sample volume consume. Kjeldahl official procedure (AOAC 1996), was used to certificate the accuracy of the sequential injection determination and, as observed in the Table 1, agreement results were obtained.

The sequential injection analysis can be considered a vanguard development of the traditional flow injection methods. Simplicity, versatility and robustness are the main characteristics offered by SIA instrumentation. The multiport valve used possibility different combinations of solutions and/or detectors around the single line configuration. Therefore two or more procedures can be adapted in the same configuration or the system fitted to a specific procedure of analysis. In comparison with traditional method, the determinations can be done with a low discharge generation and reagent consume and reduced step number. The

pervaporation unit allowed the direct soil introduction without any previous treatment simplifying the determination.

References

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(a)   (b)
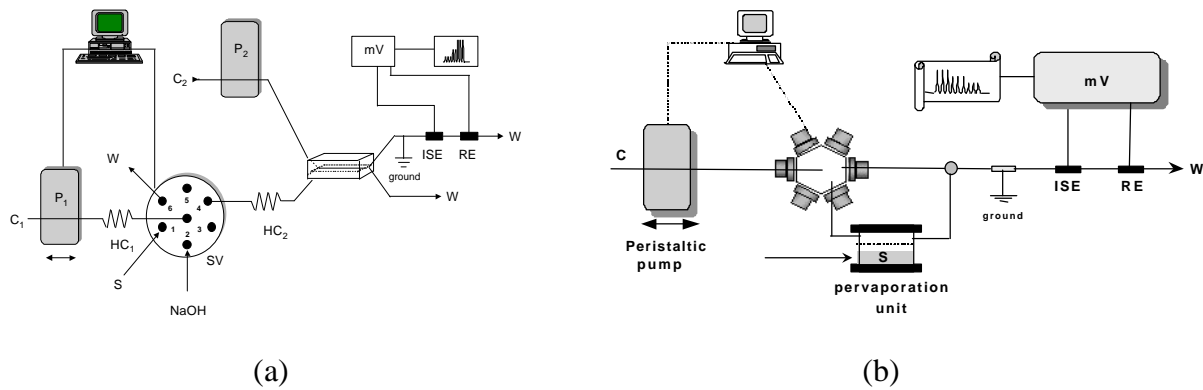
Figure 1. Sequential injection system developed for volatile nitrogen determination. (a) Silage samples: S, sample (150 µl); NaOH, alkaline solution 3.0 mol l^{-1} (300 µl); HC_1 and HC_2, holding coil (3 ml and 50 cm, respectively); C_1 and C_2, carrier streams (H_2O and TRIS-HCl buffer solution 0,01 mol l^{-1}); ISE, ion selective electrode; RE; reference electrode; P1 and P2, peristaltic pumps and W, waste. (b) Soil samples.

Table 1. Volatile nitrogen content in soil and silage sample.

Sample	Silage (g kg^{-1} N)		Soil (g kg^{-1} N)	
	SIA	Kjeldahl	SIA	Kjeldahl
1	1.19 (± 0.03)[*]	1.16 (± 0.03)	0.42	0.35
2	6.15 (± 0.09)	6.79 (± 0.11)	0.70	0.63
3	4.92 (± 0.05)	6.10 (± 0.10)	0.02	0.02

* r.s.d. (n = 3)