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"Heart-cut" column switching techniques for the determination of an aliphatic amine in an organic matrix and for low levels of sulfate in an anion matrix

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Abstract

A "dilute-and-shoot" approach to ion chromatographic analysis employing "heart-cut" column switching techniques has been demonstrated to be a powerful tool to solve a variety of analytical problems. This paper describes various refinements of this technology for a cationic "slice" method for the determination of an aliphatic amine in an organic matrix and an unprecedented example of low level anion analysis in an anion matrix: sulfate analysis in sodium phosphate.

1. Introduction

The "heart-cut" technique and its application as a tool for dealing with matrix interferences has been previously described [1,2]. This paper describes some refinements to this basic technology in an attempt to make the technique more user-friendly. The most significant problems encountered include determining retention times of the analyte on the "pre-column" in the sample matrix and dealing with the dramatic pressure changes for the analytical pump during column switching. A systematic automated approach to attaining optimal retention time parameters has been developed. The latter complication, pressure changes, is dealt with by toggling the pump off and on. It should be noted that these column switching systems may take as much as two days to fully equilibrate and analysis times can be as long as an hour; however, this technique is a powerful tool to deal with matrix interference problems and in some instances affords results that would otherwise be impossible to attain with conventional ion chromatography (IC), as well as other analytical techniques.

2. Experimental

The IC system used for the analyses was a Dionex 4500i dual channel chromatograph with an automated sampler and a pulsed electrochemical detector (PED), utilized in the conductivity mode. The aliphatic amine analyses were conducted employing three CS-3 cation-exchange columns (Dionex) with a 0.3 m*M* 2,3-diaminopropionic acid (DAP) in 10 m*M* HCl eluent at 1 ml/min. Two CS-3 columns constituted the pre-column. A single CS-3 column served as the separator column. Instrumental details of the "heart-cut" technique are described in ref. 1. The rest of the system consisted of a 200-μl loop and a CMMS Dionex suppressor with 50 m*M* tetrabutylammonium hydroxide, TBA-OH, regenerant at 3 ml/min.

The sulfate analysis in sodium phosphate was

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conducted using four AS-4A (Dionex) anion-exchange columns with a 2.0 m*M* sodium carbonate–0.75 m*M* sodium bicarbonate eluent at 1 ml/min. The pre-column and separator column were each comprised of two AS-4A columns. The rest of the system consisted of a 50-μl loop and an AMMS Dionex suppressor with 50 m*M* sulfuric acid at 3 ml/min.

2.1. Chemicals

All chemicals were Mallinckrodt AR and the water that was used was polished (deionized water further purified through a Millipore Milli-Q filtration system). The sample for the amine analysis was a large organic compound. The sample for the sulfate analysis was sodium phosphate dibasic (ACS grade).

2.2. Sample preparation

Amine sample preparation

About 1 g of sample was accurately weighed into a 100-ml volumetric flask, vigorously mixed and sonicated in about 95 ml of eluent to dissolve. The solution was allowed to cool to room temperature then diluted to volume with eluent.

Sulfate sample preparation

About 10 g of sample was accurately weighed into a 100-ml volumetric flask, vigorously mixed and sonicated in about 95 ml of water. The solution was allowed to cool to room temperature then diluted to volume with water.

3. Results and discussion

The valve configuration for the IC "heart-cut" system was previously described for sulfite analysis in food and drug items [1,2]. Fig. 1 shows the time events program for the "heart-cut" analysis. The initial configuration of the valves consists of Valve A ON, Valve B OFF. The "heart-cut" itself occurs at 5.8 min, Valve B ON. Note that the gradient pump is toggled off and back on in concert with the "heart-cut" to accommodate the dramatic change in pressure experienced by the gradient pump. The final configuration, Valve A OFF and Valve B OFF, which occurs at 7.8 min, by-passes the pre-column and completes the analysis. The system is very reproducible and works quite well once it's set up and fully equilibrated; however, good analytical results are generally not attained immediately after setting up the system. Due to minor differences in eluent or when using different columns, the parameters for the timing of the "heart-cut" will need to be optimized. The optimization process can be automated through repeated analysis with varying retention time windows of a sample with a reasonably high analyte content or a spiked sample. The optimum parameters are evaluated based on maximum peak area with minimum interference.

```
Step  Time        Description
-------------------------------------------------------
      Init        CDM-2 AutoOffset ON
      Init        CDM-2  Recorder  Mark  OFF
      Init        CDM-2 Temp.  Comp.  =  1.7 / Deg C
      Init        CDM-2 Recorder Range = 1.00 us
      Init        CDM-2  Cell  ON
      Init        CHA Heater  =  25  Deg.  C
      Init        Valve A ON
      Init        Valve B OFF
      Init        Inject Valve OFF
      Init        ACI  ASM  OFF
      Init        ACI  HLD/RS OFF
      Init        ACI  PGM+L  OFF
      Init        ACI  ON/OFF  ON
      Init        ACI  TTL  OFF
      Init        ACI  Regen ON
      Init        GPM  Start
      Init        GPM  Hold  Gradient  Clock
      Init        GPM  Reset ON
       1    0.0   ACI  ASM ON
       1    0.0   GPM  Reset  OFF
       2    0.1   ACI  ASM  OFF
       3    2.2   Inject Valve ON
       4    5.7   GPM Stop
       5    5.8   Valve B ON
       5    5.8   GPM Start
       6    7.7   GPM Run Gradient clock
       7    7.8   Valve  A  OFF
       7    7.8   Valve  B  OFF
       7    7.8   Start Sampling
       8    9.9   CDM-2 AutoOffset Off
       9   10.0   CDM-2 AutoOffset ON
```

Fig. 1. Time events program for sulfite heart-cut analysis.

A "slice" analysis consists of a "heart-cut" analysis minus the last step, late eluters to waste. The chromatograms in Fig. 2 show the effect of varying the "slice" parameters. The variable slice parameters analyses were conducted using a spiked reference sample. Fig. 3 and Table 1 show a standard additions analysis of an actual production sample using the optimized system. Attempts to develop GC or LC procedures for

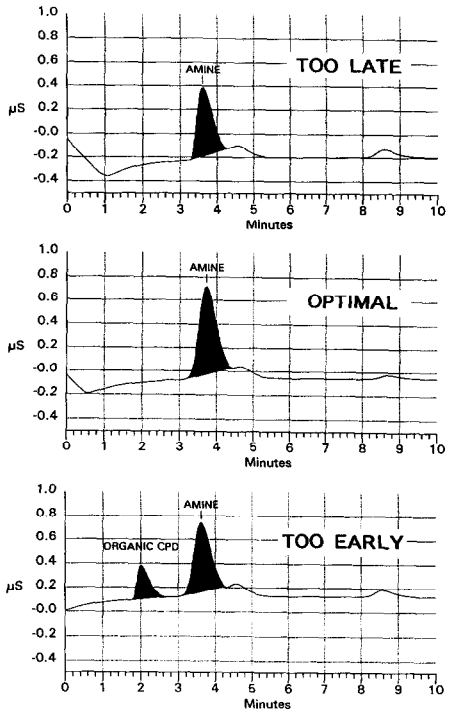

Fig. 2. Effect of varying slice parameter.

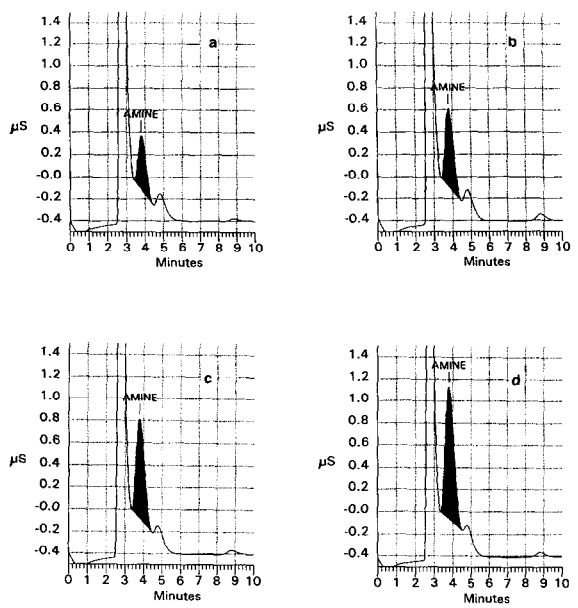

Fig. 3. Amine spikes in organic compound. (a) Unspiked; (b) 50 ppm; (c) 100 ppm; (d) 200 ppm.

Table 1
Standard additions analysis of amine in organic compound

	Spike (ppm)			
	0	50	100	200
	105	166	210	287
	104	167	209	290
	102	158	205	286
	106	165	205	282
	108	163	210	283
Average	105	164	208	286
S.D.	2.32	3.82	2.67	3.03
R.S.D. (%)	2.21	2.33	1.28	1.06

this analysis proved unsuccessful, as did a conventional IC approach.

ACS-grade sodium phosphate dibasic has a limit of 50 mg/kg sulfate maximum [3]. The recommended ACS test involves preparing an acidic 10% solution, adding barium chloride, digesting on a steam bath overnight, and filtering to weigh back any precipitate formed. The usual complications of gravimetric sulfate determination are further exacerbated by the limited solubility of barium phosphate. Copious amounts of precipitate are frequently formed during the filtration step. An alternative IC method was developed in response to the need for another means of analysis to referee borderline results.

An IC approach to analyze for a low level anion in an anion matrix presents a formidable analytical challenge, considering that a selective chemical pretreatment scheme to reduce the phosphate content without affecting the sulfate level has yet to be realized. A "dilute-and-shoot", mechanical, on-line sample preparation approach using "heart-cut" column switching techniques was developed in response to this challenge.

A 10% solution was chromatographed using a pre-column and a separator column, each of which was comprised of two anion-exchange columns. The bulk of the phosphate was diverted to waste. Fig. 4 shows a standard addition analysis. The chromatograms also show two upsets at about 22 and 32 min. The upsets are associated with the column switching. The first

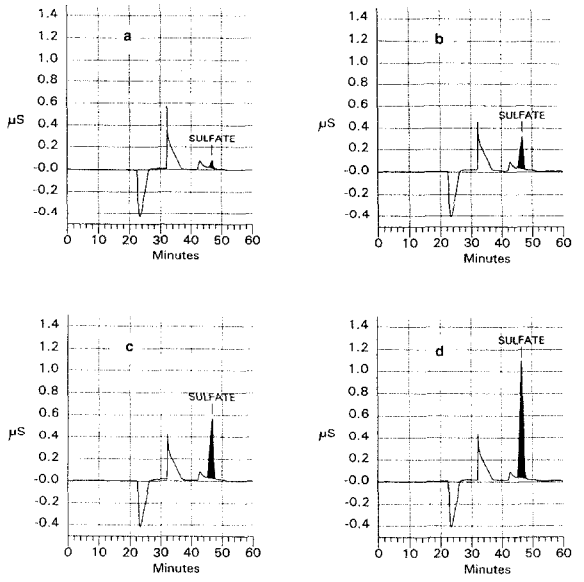

Fig. 4. Sulfate spikes in sodium phosphate. (a) Unspiked; (b) 25 ppm; (c) 50 ppm; (d) 100 ppm.

40 min of the analysis would normally not be recorded; however, the entire chromatogram was shown here to demonstrate the effect of column switching on the conductivity detector.

4. Conclusions

Our column switching technique has been demonstrated for a cationic system, namely amine analysis. Previously, only anion examples were published. The optimization of the "heart-cut" or "slice" parameters can be automated; however, the system may require a couple of days to fully equilibrate prior to optimization. A series of methods in which the retention time window of the "heart-cut" or "slice" was the only variable was used to analyze a given sample with a relatively high level of analyte present. Typically, the analyses were set-up for an overnight schedule of runs. The following day the timing of the requisite parameters were finalized and the requisite analyses begun.

The aforementioned column switching techniques for IC have been utilized to address some very difficult analytical problems. Column switching does possess some disadvantages, in particular the complexity of the system and lengthy equilibration and analysis times. These shortcomings must be weighed against alternative means of analysis, which in some cases may be non-existent.

5. Acknowledgements

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6. References

[1] S.R. Villaseñor, *Anal. Chem.*, 63 (1991) 1362–1366.
[2] S.R. Villaseñor, *J. Chromatogr.*, 602 (1992) 155–161.
[3] *Reagent Chemicals*, American Chemical Society, Washington, DC, 8th ed., 1993, pp. 696–698.