DIONEX

Application Note 104

Now sold under the Thermo Scientific brand

Thermo SCIENTIFIC

Analysis of Personal Care Products by Ion Chromatography

INTRODUCTION

Ion chromatography (IC) with conductivity detection complements traditional HPLC-UV pharmaceutical separations. IC is especially useful when the analytes do not contain chromophores, or when it is desirable to determine chromophoric and nonchromophoric molecules in a single run.

This application note addresses the use of IC for the analysis of personal care products, including compounds found in some toothpastes, hair permanent solutions, and acne medications. Several examples illustrate the variety of separations that can be achieved using IC.

Methods for analyzing fluoride, monofluorophosphate (MFP), and other phosphates present in dental care products include GC, titration, and the use of fluoride-selective electrodes.[1–3] The GC method requires derivatization of the analytes, while the other two are labor-intensive, subject to interferences, or suffer from poor reproducibility. The IC method described in this application note is a simple way to accurately quantify all of these analytes in a single, rapid run.

Another application that often requires precolumn derivatization is the determination of thioglycolic acid in hair care products.[4] IC with conductivity detection is a good choice for such organic acid analytes because it offers an alternative detection mode for nonchromophoric analytes without derivatization.

Other organic acids such as the antioxidant synergists, citrate and tartrate, are often analyzed by reversed-phase HPLC with low-wavelength UV detection. This method is troublesome because thin-layer chromatography may be required to confirm the identity of coeluting peaks.[5] However, these α-hydroxy acids can be separated efficiently on the IonPac® AS11 column with a simple hydroxide gradient, as shown in Figure 1.

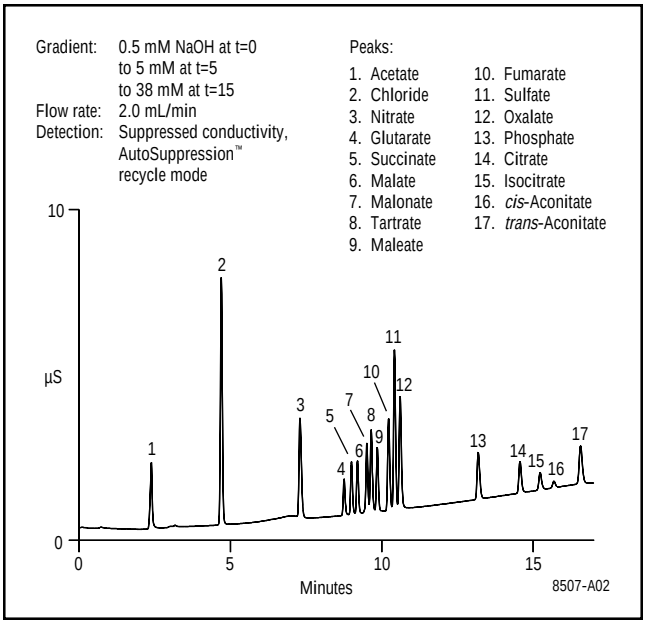

Figure 1 *Gradient separation of organic acids and inorganic anions on an IonPac AS11 column.*

The last application area addressed in this Note is the determination of salicylic acid. While this is a common reversed-phase HPLC application, IC provides an alternate separation mechanism for this compound in complex matrices, providing a "class" separation of neutral and ionic compounds. Ion-exchange separations can also provide additional information about other inorganic anions and organic acids present in the sample.

Summary of Chromatographic Methods

Most chromatograms shown were generated on the IonPac AS11 anion-exchange column (see Table 1 for conditions). The AS11 contains a solvent-compatible, high-performance anion-exchange resin with a hydrophilic latex. This hydrophilicity means that the column packing has a high affinity for hydroxide, resulting in unique selectivities.

The AS11 is the column of choice for a wide variety of applications, especially if the sample is in a complex matrix or if a gradient separation is required to separate all of the analytes. The AS11 is also recommended as an introductory methods development column for the analysis of personal care products.

EQUIPMENT

Dionex DX-500 IC/HPLC system consisting of:

- GP40 Gradient Pump
- ED40 Conductivity Detector
- AD20 Absorbance Detector
- LC20 Chromatography Enclosure
- Eluent Organizer

PeakNet Chromatography Workstation

REAGENTS

Deionized water, 17.8 MΩ-cm or better

Sodium hydroxide solution, 50% (w/w)

Acetonitrile, Fisher Optima™ grade or equivalent

PREPARATION OF REAGENTS

50 mM Sodium Hydroxide Eluent

Degas 1 L of deionized water by applying a vacuum for 15 minutes while sonicating. Add 2.6 mL of 50% sodium hydroxide and mix well. Pressurize with helium.

200 mM Sodium Hydroxide Eluent

Degas 990 mL of deionized water by applying a vacuum for 15 minutes while sonicating. Add 10.4 mL of 50% sodium hydroxide and mix well. Pressurize with helium.

Table 1 Experimental conditions

Dental Care Products

Column:	IonPac AS11 Analytical, 4 mm		
	IonPac AG11 Guard, 4 mm		
Eluents:	A = DI water		
	B = 200 mM NaOH		
Gradient:	Time (min)	A (%)	B (%)
	0	95	5
	0.2	95	5
	3.5	90	10
	10	60	40
Flow Rate:	2.0 mL/min		
Inj. Volume:	25 µL		
Detection:	Suppressed conductivity		
Suppression:	ASRS™ recycle mode		

Salicylic Acid and Excipient Anions

Column:	IonPac AS11 Analytical, 4 mm			
	IonPac AG11 Guard, 4 mm			
Eluents:	A = DI water			
	B = 200 mM NaOH			
	C = Acetonitrile			
Gradient:	Time (min)	A (%)	B (%)	C (%)
	0	90	5	5
	2	90	5	5
	20	—	50	50
Flow Rate:	1.0 mL/min			
Inj. Volume:	25 µL			
Detection:	Suppressed conductivity UV, 214 nm			
Suppression:	ASRS external water mode			

Thioglycolic Acid

Column:	IonPac AS11 Analytical, 4 mm			
	IonPac AG11 Guard, 4 mm			
Eluents:	A = DI water			
	B = 50 mM NaOH			
	C = 200 mM NaOH			
Gradient:	Time (min)	A (%)	B (%)	C (%)
	0	95	5	—
	2	95	5	—
	20	17	83	—
	20.01	50	—	50
Flow Rate:	1.0 mL/min			
Inj. Volume:	25 µL			
Detection:	Suppressed conductivity			
Suppression:	ASRS external water mode			

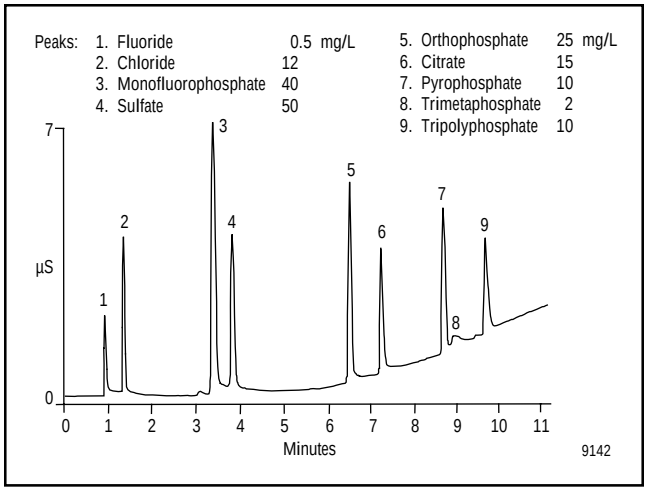

Figure 2 *Separation of toothpaste additives. See Table 1 for conditions.*

DISCUSSION AND RESULTS

In addition to yielding different types of information about ingredients in personal care products, IC offers the pharmaceutical chemist column efficiencies and method performance equivalent to traditional HPLC.

The IonPac AS11 has a highly crosslinked core, making it solvent-compatible and able to withstand high pressures. The thin monolayer of ion-exchange latex that is agglomerated to the surface of this core provides good mass transfer, which translates into very high efficiency separations.

Dental Care Products

Monofluorophosphate is the active ingredient in some brands of fluoridated toothpaste. The MFP breaks down to fluoride and both can be chromatographed in the same run (see Figure 2).

Polyphosphates, also commonly found in these types of products, are traditionally difficult to chromatograph. They have high affinities for anion exchange resins and require very high eluent concentrations that can exceed the capacity of the suppressor. Due to the affinity of the AS11 for the eluent ion hydroxide, however, the higher valency polyphosphates elute at much lower concentrations of hydroxide, as shown in Figure 2.

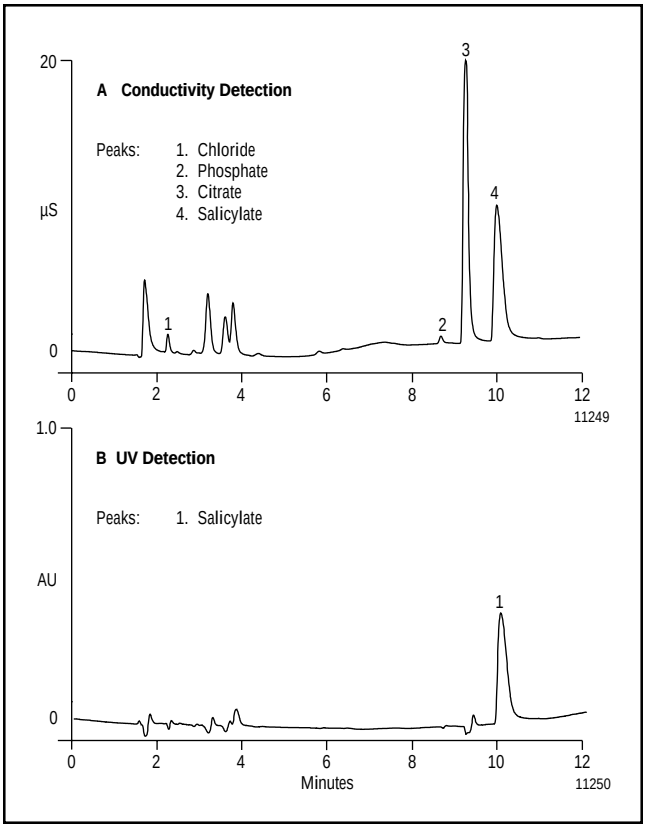

Figure 3 *Separation of salicylic acid and other anions in acne medication. A = Conductivity detection; B = UV Detection at 214 nm. Sample (1 g) was dissolved in 100 mL of water prior to injection. See Table 1 for conditions.*

Salicylic Acid and Excipient Anions

Figure 3 shows the analysis for salicylic acid, organic acids, and inorganic anions in an over-the-counter acne medicine.

Salicylate, the active ingredient in this formulation, is routinely chromatographed using reversed-phase HPLC. However, using IC with conductivity detection, other common excipients such as chloride, phosphate, and citrate anions can be quantified in the same run (see Figure 3A).

By contrast, the UV profile of this sample (see Figure 3B), regardless of the separation mechanism, does not allow quantification of these nonchromophoric anions.

Thioglycolic Acid

Thioglycolic acid is the active ingredient in home hair permanent waving solutions, as well as some depilatory creams. Figure 4 shows a chromatogram of a waving solution.

Because the waving solution was injected onto the column with no pretreatment, a high ionic strength column flush step was programmed for the end of every run. This helped prevent build-up of other product ingredients, such as surfactants, on the column. Recovery of thioglycolate using this method was 96% and area reproducibility was 1.8% (n=8).

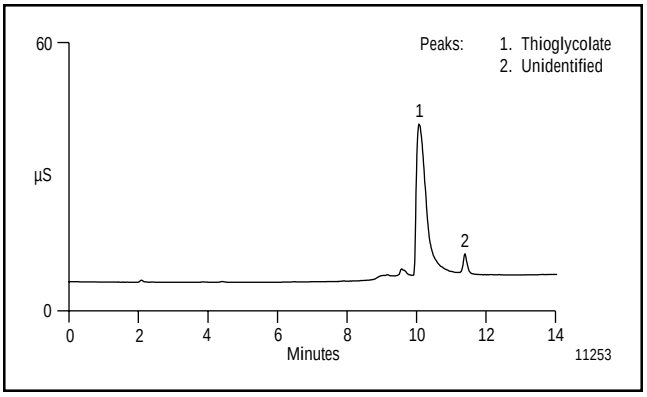

Figure 4 *Thioglycolic acid in a home permanent waving lotion. Sample was a 1/250 suspension in water. See Table 1 for conditions.*

Alternative Columns

Although the AS11 is recommended for sample screening work, other columns in the IonPac family can often be employed once feasibility has been established.

For example, Figure 5 shows MFP, fluoride, and other anions found in a dental care product chromatographed using an IonPac AS12A column. Unlike the AS11 run in Figure 2, many of these analytes can be chromatographed isocratically using the AS12A column. An additional benefit of the AS12A separation is that the fluoride peak is well separated from the system void, which makes quantification of fluoride easier.

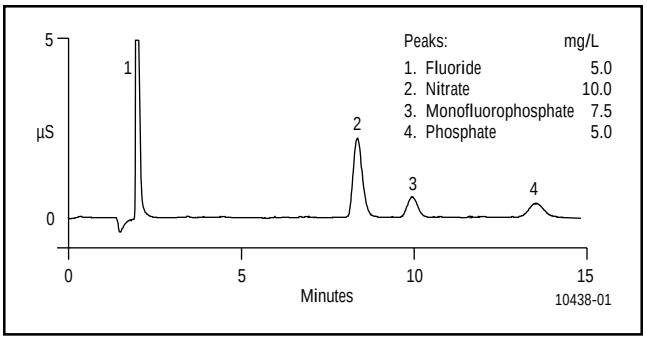

Figure 5 *Anions found in toothpaste were separated on the IonPac AS12A column. Eluent was 2.5 mM sodium carbonate/ 0.8 mM sodium hydroxide at 1.5 mL/min. Conductivity detection with AutoSuppression in the recycle mode was used.*

Figure 6 shows an alternative separation for organic acids. The IonPac ICE-AS6 column is a good choice for organic acid analysis when the number of analytes is limited and when high concentrations of inorganic anions, such as chloride, interfere with ion-exchange analysis. Because this column uses ion exclusion as the separation mechanism, any strong acid inorganic anions will elute in the excluded volume at the beginning of the chromatogram.

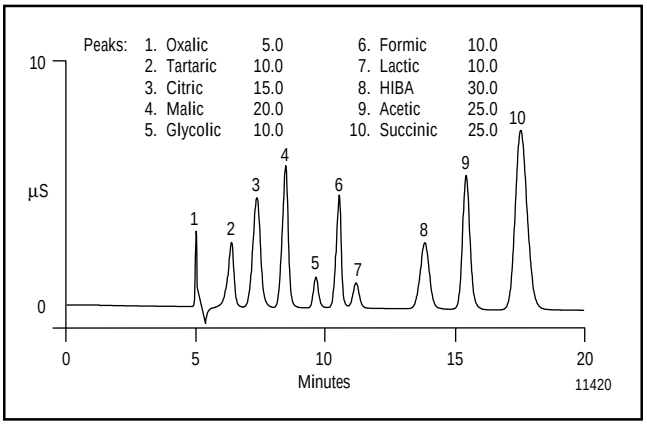

Figure 6 *Separation of organic acids by ion exclusion on the IonPac ICE-AS6 column. Eluent was 0.4 mM heptafluorobutyric acid at 1.0 mL/min. Conductivity detection with an AMMS™-ICE suppressor was used with 5 mM tetrabutylammonium hydroxide as the regenerant.*

REFERENCES

1. Official Journal of the European Communities, **1983**, No. L 291/37–40.
2. Borissova, R.; Debouki, A.; Nikolov, T. *Fresenius' J. Anal. Chem.* **1993**, *347*, 63–66.
3. Hattab, *J. Dent.* **1989**, *17*, 77–83.
4. Cavrini, V.; Andrisano, V.; Gatti, R.; Scapini, G. *Int. J. Cosmet. Sci.* **1990**, *12*, 141–150.
5. Irache, J.M.; Ezpeleta, I.; Vega, F.A. *Chromatographia* **1993**, *35*, 232–236.

Dionex Corporation
1228 Titan Way
P.O. Box 3603
Sunnyvale, CA
94088-3603
(408) 737-0700

Dionex Corporation
Salt Lake City Technical Center
1515 West 2200 South, Suite A
Salt Lake City, UT
84119-1484
(801) 972-9292

Dionex U.S. Regional Offices
Sunnyvale, CA (408) 737-8522
Westmont, IL (630) 789-3660
Houston, TX (281) 847-5652
Smyrna, GA (770) 432-8100
Marlton, NJ (609) 596-0600

Dionex International Subsidiaries
Austria (431) 616 51 25 *Belgium* (015) 203800 *Canada* (905) 844-9650 *France* 01 39 46 08 40 *Germany* (06126) 991-0
Italy (6) 66030052 *Japan* (06) 885-1213 *The Netherlands* (076) 57 14 800 *Switzerland* (062) 205 99 66 *United Kingdom* (01276) 691722
* Designed, developed, and manufactured under an NSAI registered ISO 9001 Quality System.

http://*www.dionex.com*

LPN 0657-01 3.5M 6/97