Poster Note 71972

Determination of Aluminum in Over-the-Counter (OTC) Products

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Overview

Purpose: To develop and validate an ion chromatography (IC) method for the determination of aluminum in OTC products.

Methods: The separation is achieved using a Thermo Scientific™ Dionex™ IonPac™ CS10 analytical column with detection by postcolumn addition of Tiron, a colorimetric reagent, followed by measurement of UV absorbance at 310 nm.

Results: An IC method was successfully developed and validated for determination of aluminum in two OTC products; antiperspirants and antacids.

Introduction

Aluminum (Al) is the most abundant metallic element in the earth's crust.[1] It is mainly found as oxides or silicates (oxidation state +3). Aluminum-containing compounds are used extensively in cosmetics, prescription pharmaceuticals, and OTC drug products. A number of aluminum-containing compounds are used as active ingredients in underarm antiperspirant products. Compounds approved for this purpose do not include alumina or aluminum hydroxide. However, aluminum zirconium octachlorohydrate and aluminum chlorohydrate can be used at concentrations up to 20% and 25% by weight, respectively, in the United States and Europe. Aluminum chloride can be used in antiperspirant products at concentrations up to 15% in Europe. The U.S. FDA allows OTC sale of antiperspirants containing 15–25% aluminum (with the amount varying based on the specific compound used). In general, most OTC antiperspirants contain some form of aluminum-based compound as the main active ingredient—mostly aluminum chloride or aluminum chlorohydrate. Aluminum salts in antiperspirants dissolve in the moisture on the skin surface and form a gel, creating a small temporary 'plug' on the sweat gland and reducing the amount of sweat that is secreted to the skin surface.[2]

Aluminum-based compounds are also used in antacid formulations. Aluminum hydroxide and magnesium hydroxide act as antacids by neutralizing stomach acid that results in an increased pH in the stomach.

The United States Pharmacopeia (USP) has adopted several different assays for aluminum in various OTC products. The analytical techniques used include complexometric titration, chelatometric titration, ion-exclusion chromatography, and reversed-phase liquid chromatography. The choice of assay method is often predicated by the dosage form. Aluminum can be determined using ion chromatography (IC) with an easy setup and fast run time. Dionex (now part of Thermo Fisher Scientific) Application Note (AN) 69 describes the determination of aluminum in complex matrices using chelation ion chromatography.[3] AN69 uses a Thermo Scientific™ Dionex™ IonPac™ CS5 column for the separation of aluminum from other cations and postcolumn derivatization for detection by UV absorbance.

Here, we report the development and validation of an IC method for the determination of aluminum in OTC products (shown below) with a cation-exchange column and postcolumn derivatization prior to UV absorbance detection. Figure 1 shows the diagram of instrumental setup used in this study. The separation is achieved using a Dionex IonPac CS10 analytical column with detection by postcolumn addition of Tiron (4,5-Dihydroxy-1,3-benzenedisulfonic acid), a colorimetric reagent, followed by measurement of UV absorbance at 310 nm. The method was evaluated in terms of linearity, precision, accuracy, ruggedness, and limit of quantitation for aluminum. For more details please refer to the application note AN 1142 on the Thermo Fisher Scientific website.[3]

Antacid suspension

Antiperspirant solid stick

Methods

System set up and configuration

Below is the schematics showing the IC system configuration for the determination of aluminum using post column derivatization followed by UV detection. Please refer to TN 26 for more details.[4]

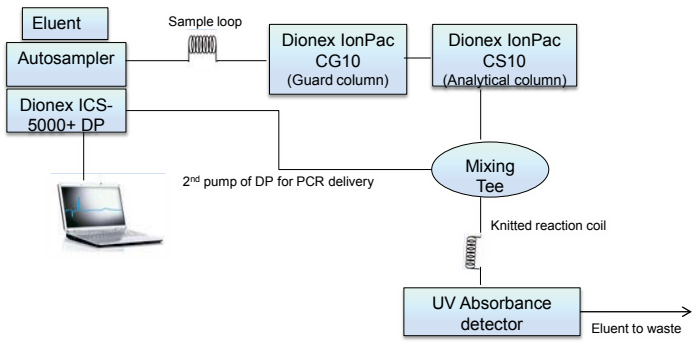

TABLE 1. OTC samples used in this study.

	Sample	Formulation	Active ingredient
1	Antiperspirant	Solid stick	Aluminum Chlorohydrate
2	Antiperspirant	Solid stick	Aluminum Zirconium tetrachlorohydrex
3	Antacid	Suspension	Aluminum Hydroxide

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Sample Preparation

Antiperspirant Sample

Step 1. Accurately weigh 150 mg of deodorant powder sample into a 25 mL volumetric flask.

Step 2. Add 25 mL of 50 mM NaOH, cap, and vigorously shake for 5–10 min.

Step 3. Sonicate the solution from Step 2 for 30 min.

Step 4. Dilute it 20 times using 50 mM NaOH and then pass the liquid through a Nalgene syringe filter before analysis.

Antacid Sample

Step 1. Accurately weigh 250 µL of antacid suspension into a 25 mL volumetric flask.

Step 2. Add 25 mL of 50 mM NaOH, cap, and vigorously shake for 5–10 min.

Step 3. Sonicate the solution from Step 2 for 30 min.

Step 4. Dilute it 20 times using 50 mM NaOH and then pass the liquid through a Nalgene syringe filter before analysis.

Note: All the samples and standards used in this study are prepared in 50 mM NaOH. Aluminum chloride ($AlCl_3 \cdot 6H_2O$) is used to prepare the aluminum standard.

Sample Analysis

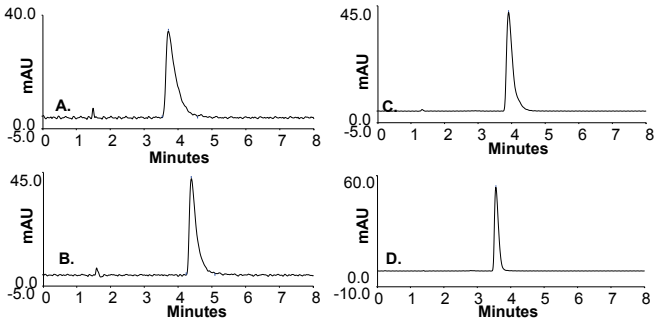
Thermo Scientific™ Dionex™ Chromeleon™ 7.1 Chromatography Data System (CDS) software was used for data collection and processing.

Results

Separation

There have been numerous improvements in cation exchange columns for IC since the publication of AN69,[5] the following cation-exchange columns— Dionex IonPac CS5A, Thermo Scientific™ OmniPac™ PCX-100, Dionex IonPac CS11, and Dionex IonPac CS10 columns—were evaluated to replace the Dionex IonPac CS5 column for this analysis. Figure 2 shows chromatograms of a 20 mg/L aluminum standard on Dionex IonPac CS5A, OmniPac PCX-100, Dionex IonPac CS11, and Dionex IonPac CS10 columns, respectively. Among these columns the Dionex IonPac CS10 column gave the best result in terms of peak shape, peak symmetry, and loading capacity.

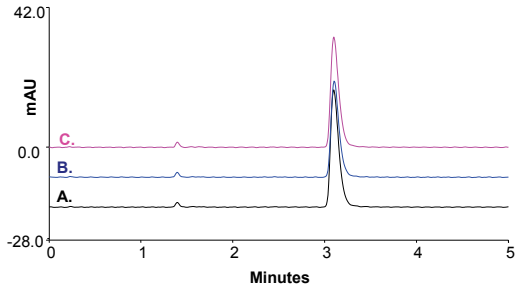
FIGURE 2. Chromatogram of 20 mg/L Aluminum standard on A. Dionex IonPac CS5A , B. IonPac CS11 C. OmniPac PCX100 and D. IonPac CS10 columns



Sample analysis

An antacid suspension and two antiperspirant sticks were purchased from a pharmacy and analyzed for their aluminum content. Samples used in the study were found to be only slightly soluble in water. After the solution was kept for 2–3 days, the sample tended to settle at the bottom, giving incorrect aluminum concentrations. Various concentrations of different acids and bases were tested to improve the dissolution of the aluminum sample and 50 mM NaOH was chosen for this work as it gave the best solubility. Thus all samples and standards were prepared in 50 mM NaOH instead of DI water. The concentration range for aluminum as calculated in antiperspirant /antacid samples was approximately 200–250 mg/L for 150 mg/250 µL sample dissolved in 25 mL of 50 mM NaOH. To avoid overloading the column, antiperspirant and antacid samples were diluted 20 times with 50 mM NaOH before analysis. Figure 3 shows chromatograms of samples (Antiperspirant 1, Antiperspirant 2, and Antacid 1) containing aluminum on a Dionex IonPac CS10 column.

FIGURE 3. Chromatogram of A) Antiperspirant 1; B) Antiperspirant 2; and C) Antacid 1 sample on a IonPacCS10 column

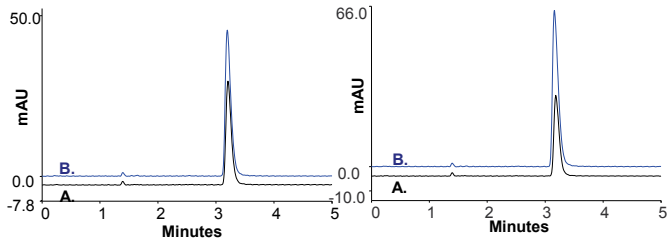


Sample Recovery

Antacid sample

Method accuracy was evaluated by calculating the recovery of aluminum after spiking directly into the antacid and antiperspirant samples at 50% and 100% of the expected amount. Samples were prepared and injected in triplicate. Figures 4 show an overlay of the spiked and unspiked antacid sample. Recoveries for aluminum spiked at 50% and 100% of the expected amount into the antacid sample were 99.9% and 100%, respectively (Table 2).

FIGURE 4 Left. Chromatogram of A) Antacid 1 sample and B) spiked Antacid 1 sample (spiked 50% of sample). **Right.** Chromatogram of A) Antacid 1 sample and B) spiked Antacid 1 sample (spiked 100% of sample).



Antiperspirant samples

Figures 5 and 6 show an overlay of the spiked and unspiked antiperspirant samples, respectively. For antiperspirant samples recoveries were 78.1–80.7% and 74.7–104%. A reason for the low recoveries of aluminum in antiperspirant samples could be the sticky nature of the sample, which tends to make it cling to the bottom or sides of the flask giving inconsistent results. Another reason could be possible non-uniformity of aluminum content in the antiperspirant stick.

FIGURE 5 Left. Chromatogram of A) Antiperspirant 1 sample and B) Spiked antiperspirant 1 sample (spiked 50% of sample). **Right.** Chromatogram of A) Antiperspirant 1 sample and B) Spiked antiperspirant 1 sample (spiked 100% of sample)

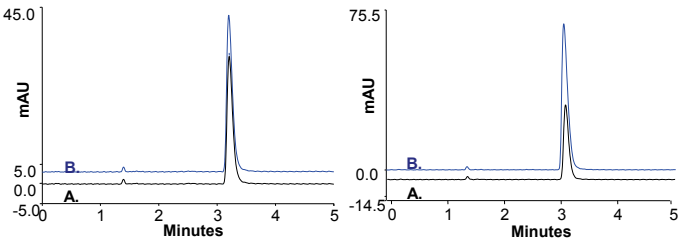


FIGURE 6 Left. Chromatogram of A) Antiperspirant 2 sample and B) Spiked Antiperspirant 2 sample (spiked 50% of sample). **Right.** Chromatogram of A) Antiperspirant 2 sample and B) Spiked Antiperspirant 2 sample (spiked 100% of sample).

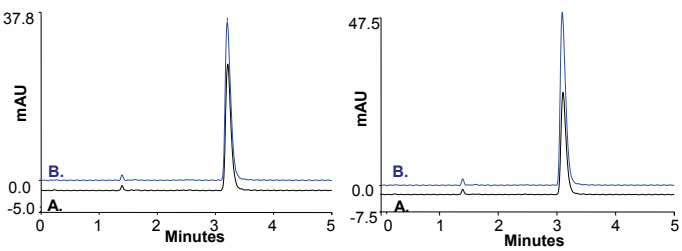


TABLE 2. Results of spike recovery for aluminum in antiperspirant and antacid samples.

Sample	Spike Level	Found (mg/L)	Added (mg/L)	Recovered (mg/L)	Recovery (%)
Antacid 1	+50%	9.66	5.21	14.9	99.9
	+100%	9.82	9.53	19.4	100
Antiperspirant 1	+50%	10.2	4.77	13.0	80.7
	+100%	10.7	13.3	24.4	104
Antiperspirant 2	+50%	8.40	4.75	11.3	78.1
	+100%	8.68	7.23	13.5	74.7

Note: Due to the insolubility of aluminum oxide in aqueous solution, this method is not applicable to the OTC products containing aluminum oxide as an active ingredient.

Conclusion

- Here we presented the successful determination of aluminum cation in OTC products.
- Two types of OTC products: antacid and antiperspirant were analyzed. For antacid, a suspension formulation was used, and for antiperspirant, solid sticks were used.
- Spike recoveries for the antacid sample are 99–101% and 75–110% for the antiperspirant samples.

References

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