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ION CHROMATOGRAPHIC DETERMINATION OF ANIONS COLLECTED ON FILTERS AT ALTITUDES BETWEEN 9.6 AND 13.7 KILOMETERS

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ERRATA

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PAGE	LINE	
1	18	Insert "10" after "model".
3	5	Insert "1" after ">".
3	19	Replace "It" by "this peak".
5	22	Add "to extract" after 10 ml. of element".
8	17	Replace "Only" by Mostly and delete "be able to".
10	19	Add "filters" after "some".

ION CHROMATOGRAPHIC DETERMINATION OF ANIONS COLLECTED ON FILTERS AT ALTITUDES BETWEEN 9.6 AND 13.7 KILOMETERS

BY

DUMAS A. OTTERSON

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The NASA Global Air Sampling Program (GASP) is an investigation of atmospheric pollution at altitudes generally used by jet-liners. Part of this investigation is concerned with anion-containing particulates in the atmosphere at altitudes between 9.6 and 13.7 km. The samples are collected on cellulose fiber discs which have been impregnated with dibutoxyethylphthalate. These filters have good retention for particulates and are designed for high altitude air sampling (Ref. 1&2). Less than 30 micrograms (μg) of any one anion is collected on a sample because of limitations in the amount of air than can be filtered during a commercial jet-craft flight. Hence, very sensitive methods of analysis are required for this study.

Ion chromatography with eluent suppression and conductometric detection enables more thorough investigations of anions in the atmosphere than previous methods. This instrument was first described by Small, Stevens, and Bauman (Ref. 3) Their paper indicates that at least 29 anions can be detected in submicrogram amounts. Most of the anions can be determined in about 20 minutes in a single chromatogram.

A Dionex Model Ion Chromatograph* designed for anion analysis is used in the GASP investigation. A similar unit and its use have been dis-

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* Mention of a specific product or company does not consitute endorsement by the National Aeronautics and Space Administration.

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cussed in detail by Mulick, Puckett, Williams and Sawicki (Ref. 4). Our preliminary work indicated that a sensitivity close to 0.001 ppm of an anion in solution should be obtainable. It is very difficult to attain these high sensitivities. Contamination and side reactions are the chief causes for loss of sensitivity. The factors that have been controlled to achieve the sensitivity needed for the determination of microgram amounts of F^-, Cl^-, NO_3^- and $SO_4^=$ will be discussed.

EQUIPMENT

Dionex Model 10 Ion Chromatograph
- Sample loop - 500 µl
- Separator Column - 3x500 mm - filled with Chromex DA-x5-0.376(127C) resin
- Suppressor Column - 6x250 mm - filled with Chromex DC-x12-55 resin
- Pumping Speed - 1.3 ml per minute

Glassware
- 5 ml syringe - to transfer extract to sample inlet on ion chromatograph
- 10 ml syringe - to transfer eluent to extract ion bottle
- bottles - 30 ml - equipped with ground glass cap that fits around neck of bottle

Hypodermic needle - 3-inch - blunt end - with standard female Luer hub

(A wad of cotton is placed on a wire coil inside the needle hub. It is the means of removing filter paper lint from the extract.)

REAGENTS

Eluent - (Mixture composed of 0.003M $NaHCO_3$+0.0024 M Na_2CO_3)

$NaHCO_3$ - Reagent Grade

Na_2CO_3 - Reagent Grade

Acetone - Electronic Grade

Water - Deionized (resistivity >7megohm)

Organic materials removed by activated charcoal column.

Air Stream - Purified in a column of molecular sieve (Linde 13x) and a 10 micron mesh metallic filter

PURIFICATION OF EQUIPMENT

All surfaces that could possibly contaminate the extraction solution are cleansed and dried after each use. This includes the less obvious surfaces such as the ground glass surfaces of the bottle, its stopper, and the syringe, as well as the hypodermic needle and cotton wad. These items are rinsed with eluent, then three times with deionized water and finally with acetone. They are dried using a stream of purified air. Acetone should be removed as completely as possible. It can interfere with the Cl^- determination. It produces a peak whose elution time is slightly greater than that of the chloride ion. It can overlap the Cl peak if too much remains in the glassware. If the glassware contains relatively large amounts of anion, it may be necessary to use a stronger buffer in order to expedite its purification. In this event more extensive rinsing could be needed. During washing, the syringe plunger should be held by a metal holder to avoid contamination of the wash liquids by contact with one's fingers. Blanks are run each day in order to evaluate the purity of the system. If a blank is too high, no determinations are done until blanks indicate that the source of contamination has been eliminated.

The filters (7.6 cm diameter) are purified individually in room air prior to being used to collect the sample from the atmosphere. Vacuum is used to remove the liquids from the filter resting on a sintered glass Buchner funnel. The purification steps include soaking in a carbonate buffer solution (0.3 M $NaHCO_3$ and 0.24 M Na_2CO_3) and then in 1 M acetic acid, rinsing thoroughly with six portions (30 to 35 ml) of deionized water which is saturated with dibutoxyethylphthalate. The filters are then dried at room temperature in vacuum over KOH pellets. Variations in purity of the washed filters can result from differences in the contamination due to dust as well as differences in the treatment.

PROCEDURE

The blanks and the anion content of the filters are carried out in the same way except that one-fourth of a filter is added to the bottle before adding the eluent if a sample is to be analyzed. The procedure is as follows:

10 ml of eluent are added to the clean and dry bottle. The bottle is shaken, allowed to stand a few minutes and shaken again. 2.5 to 3.0 ml of the extract are drawn through the cotton filter in the needle into a clean and dry 5 ml glass syringe. This solution is used to rinse the inlet and sample loop of the chromatograph and to fill the loop. The

contents of the 0.5 ml sample loop are injected into the eluent stream for the determination of anions. Strip chart recordings similar to the one in Figure 1 are obtained.

DISCUSSION

Investigations of the anion content of the atmosphere at altitudes between 9.6 + 13.7 km requires either more sensitive analytical techniques or much larger samples than are used for similar investigations of the atmosphere close to the earth's surface. Pollution of the upper atmosphere is much less than in the air at the lower altitudes. Ion chromatography is well suited for investigations of the anion content of the atmosphere at higher altitudes. Methods for the determination of a number of anions by this technique can be very sensitive and rapid contamination and interfering side reactions must be controlled in order to determine microgram quantities of anions collected on filters.

Ion Chromatographic Determination of Anions. The sensitivity and the speed with which anions can be determined in a solution by ion chromatography is indicated by Figure 1. It is a typical strip chart recording of the response of the ion chromatograph as a function of time. It reveals that F^-, Cl^-, NO_3^-, and SO_4^{-2} can be determined in an aqueous sample in about twenty minutes. The height of the peaks implies that 0.001 ppm of an anion could be detected if the most sensitive setting (x.1) of the instrument were used.

Determination of Anions on Filters. The GASP method uses 10 ml of eluent anions from one-fourth of the filter. The use of eluent for this purpose avoids interference with F^- + Cl^- that is caused by a negative peak.

This peak is obtained if the extracted sample contains much less carbonate and bicarbonate than the eluent. Inasmuch as the extract is injected into the ion chromatograph, the detection limit of the method should be near 0.04 micrograms of an anion per filter. This sensitivity is difficult to attain because of contamination and interfering side reactions.

Contamination and Interfering Reactions. Most of the contamination and the interfering reactions occur during the extraction of anions from the filter and the transfer of the extract to the ion chromatograph. Extraction by the eluent appears to be complete in a few minutes. This extraction method was so effective that apparently clean glassware and filters were sources of contamination. The cleaning procedures which were adequate for other determinations of anions on these filters needed to be improved for this method. Experiments were carried out which led to a concept that explains a number of seemingly unrelated phenomena as well as to new purification methods.

The concept implies that exchange reactions which take place on anion exchange resins also occur on glass and on cellulose surfaces. All three surfaces contain more or less active hydroxyl groups (or other anions which had displaced these groups). These are assumed to be the active exchange sites. This similarity in surface compositions of these materials provides some theoretical support for this concept.

Two types of evidence suggest that exchange reactions occur on glass. In one instance, 10 ml of eluent removed 20 micrograms of NO_3^- from the inner surface of a glass bottle after seven thorough rinsings with deionized water. Rough calculations indicate that all of this NO_3^- could have been adsorbed at hydroxyl exchange sites on the inner surface of the bottle. This suggests that competitive exchange between the carbonates and NO_3^- could have occurred at these sites and the effective cleaning mechanism is due to carbonate ions displacing the NO_3^- from these sites. Similar behavior has often been observed after the bottle contained solutions with relatively high anion concentrations. That is, the eluent was able to remove measurable amounts of anions which remained after thorough rinsing with water.

Table I presents data that could be due to Cl^- being retained on exchange sites. An HCl solution was added to platinum, glass and the filter. They were all vacuum dried at room temperature. Both the filter and glass retained measurable amounts of Cl^-. Platinum which has no surface hydroxyl groups did not. These results suggest that a filter sample could also include a measurable amount Cl^- from gaseous air contaminants. More experimentation is needed to establish the retention mechanism and to learn the capacity of the filters for the retention of this type of Cl^-.

The similarity in behavior of glass and cellulose fiber filters such as indicated by this evaporation study is also found when the extraction of anions by deionized water is compared with that due to the eluent. As in the case of glass, extensive washing by pure water allows the filters to retain measurable amounts of anions. These are readily extracted by 10 ml of eluent. This supports the contention that competitive exchange reactions occur on filter surfaces. These reactions could readily account for the rapid extraction of anions from the filter by the eluent. Competitive exchange reactions on anion exchange resins is the reaction fundamental to ion chromatography. Ion chromatographic results may provide guidance in the treatment of glassware and cellulose. Indeed, the washing procedures for the glassware as well as the filters are based in part on this concept.

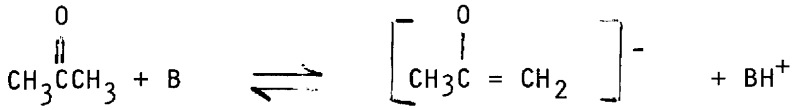
Table II indicates the degree of purity of the equipment that can be achieved by these cleaning procedures as well as the error that can be expected from differences. It presents the average values, $\bar{x}$, of the blanks for F^-, Cl^-, NO_3^-, and SO_4^{-2} obtained over a five-week period and the standard deviations for these values. Little error should be due to contamination of the equipment if the procedures are followed.

Table III reveals a much greater contamination of the washed filters as well as greater differences in purity of the various filters. It shows the average amount of F^-, Cl^-, NO_3^-, and SO_4^{-2} found on ten filters which were washed over a five-month period. Improved washing techniques are needed to reduce the error in analyses of the anions collected on filters.

Equipment to purify large numbers of filters simultaneously is now being constructed. Mostly ~~Only~~ purified air will ~~be able to~~ contact the filter. This is expected to provide uniformly pure filters in good supply. These will be needed for a more thorough study of the reliability of this method of analysis as well as for an improvement in the accuracy of analyses.

<u>Interfering Reactions</u>. Some organic compounds react with the eluent to form anions which can be detected by ion chromatography. Serious interferences with anion determinations may occur if organic compounds are present in the sample. For instance, low molecular weight alcohols can be detected if present in the eleunt. Apparently the alcoholate ions are formed. The

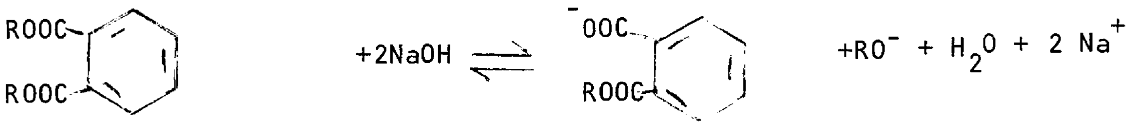
interference due to acetone which was mentioned previously may be due to its enol form. The enolization of acetone can be written:



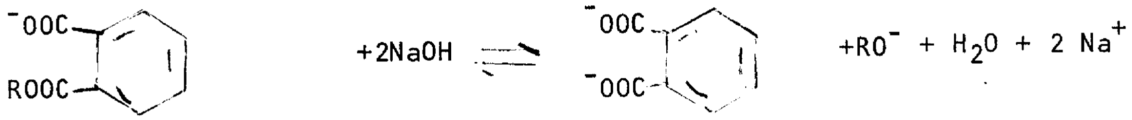
$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + B \rightleftharpoons \left[CH_3\overset{O}{\overset{|}{C}} = CH_2\right]^- + BH^+ \quad (1)$$

where B is an alkaline substance.

Interferences with the $F^- + Cl^-$ determinations are caused by reactions involving dibutoxyethylphthalate. These interferences were discovered when the peaks for these ions increased on aging of filter extracts. It was soon learned that this occurred with all solutions that contained both the eluent and dibutoxyethylphthalate. The NO_3^- and SO_4^{-2} peaks remained constant. When a more dilute eluent was used, the elution times were extended sufficiently to indicate that the increase was caused by interfering substances. Dibutoxyethylphthalate is an ester. Esters saponify in alkaline solutions. If this ester saponifies in two steps, saponification products could be the sodium salt of butoxyethanol, sodium monobutoxyethylphthalate, and sodium phthalate. The reactions which could yield these substances are:



(2)



(3)

where R stands for the butoxyethyl group ($C_4H_9OC_2H_5$). The sodium salt of butoxyethanol was found to elute with the F^- ion. Phthalate ion requires much longer elution times than any of the anions of interest. Some evidence indicates that the Cl^- interference decreases when phthalate ion increases. Hence, sodium monobutoxyethylphthalate appears to be the cause of the Cl^- interference. If so, this implies that dibutoxyethylphthalate does saponify in two steps in a mildly alkaline solution such as the eluent.

Circumventing Saponification Interference. Because saponification is relatively slow, reasonably accurate results for $F^- + Cl^-$ can be obtained for IPC 1478 filters even though they do contain dibutoxyethylphthalate. Figure 2 shows the apparent increase in $F^- + Cl^-$ content as a function of time that elapsed between mixing of the eluent with a filter and injection of the extract into the ion chromatograph. These data indicate that errors due to saponification increase significantly with aging. The values indicated by extrapolation to the time of mixing is the amount of F^- or Cl^- on the filter if several assumptions are valid. The first assumption is that the rate of saponification is almost constant during the time period involved. The results obtained for 3 data points imply that this assumption is valid. The second is that no saponification products are on the filter at the start of the extraction. This means that the method cannot be used if IPC 1478 filters contain alkaline additives. For instance, tetrabutylammonium hydroxide has been added to some filters to improve their collection efficiency for acid gases such as HCL. Hence, these filters contain large amounts of the saponification products. The third assumption is that F^- and Cl^- are extracted quantitatively during the first aging period. One can infer that extraction of F^- and Cl^- is complete from the evidence that NO_3^- and SO_4^{-2} do not increase upon aging of the filter in the eluent. These two anions have much longer elution times than F^- and Cl^-. If the anion exchange sites of cellulose and anion exchange resins are indeed the same, then these halide ions should be extracted from the filter faster than NO_3^- or SO_4^{-2}. This assumption is also supported by the data of Table IV. The agreement is close to the limits expected from the variation in anion content of washed filters (see Table III). A more definitive study of the reliability of these procedures is being delayed until a large number of filters with uniform purity are available.

CONCLUDING REMARKS

Ion chromatography is uniquely suited for the determination of anions collected on filters. It is rapid and thorough. An attribute of ion chromatography that is significant in environmental studies is its ability to indicate the presence of unsuspected anions. The presence of measurable amounts of F^- on our filters was not considered until it was identified as the cause of one of the peaks obtained in the analyses of the filter extracts. More work may be required to establish the validity of this identification. However, the possibility that F^- might be included in our investigation of the upper atmosphere may be quite significant in view of the freon controversy.

Contamination and interfering side reactions must be controlled to utilize the ultimate sensitivity of ion chromatography. The control of these factors to the extent necessary for the determination of microgram quantities of anions on cellulose filters has been discussed. Evidence was presented to support the view that glass and cellulose surfaces are sites of the same competitive anion exchange reactions that occur on anion exchange resins.

REFERENCES

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2. Cadle, R. D.; et al.: Relative Efficiencies of Filters and Impactors for Collecting Stratospheric Particulate Matter. J. Atmos. Sci., vol. 30, no. 5, May 1973, pp. 745-747.
3. Small, Hamish; Stevens, Timothy S.; and Bauman, William C.: Novel Ion Exchange and Chromatographic Method Using Conductometric Detection. Anal. Chem., vol. 47, no. 11, Sept. 1975, pp. 1801-1809.
4. Mulik J.; et al.: Ion Chromatographic Analyses of Sulfate and Nitrate in Ambient Aerosols. Anal. Lett., vol. 9, no. 7, 1976, pp. 653-663.

TABLE I

Chloride Ion Retained by Platinum, Glass, and IPC 1478 Filters After Evaporation of HCl from their surfaces.

	Cl Retained (micrograms)
Pt	~ 0.2
Glass	1.7
IPC 1478 filter	1.5
Added as HCl	2.0

TABLE II

Daily Blanks Obtained Between August 31, 1976 and October 4, 1976.

	F^-	Cl^-	NO_3^-	SO_4^{-2}
	(microgram per filter)			
$\bar{x}$	.28	.36	.10	.42
S	.06	.14	.04	.12

$$S = \sqrt{\frac{(\bar{x} - xi)^2}{n - 1}}$$

Where n is the total number of individual values, xi.

TABLE III

Anion Content of Ten Filters Purified between
August 28, 1976 and January 21, 1977

	F^-	Cl^-	NO_3^-	SO_4^{-2}
	(micrograms per filter)			
$\bar{x}$	1.28	.88	.34	1.13
S	.66	.98	.24	.36

TABLE IV

Determination of F^- + Cl^- on IPC 1478 Filters

F		Cl	
(micrograms per filter)			
Added	Found	Added	Found
10.2	9.2	10.7	10.5
10.2	9.4	10.7	10.5
		8.3*	8.3

* HCL added instead of NaCl

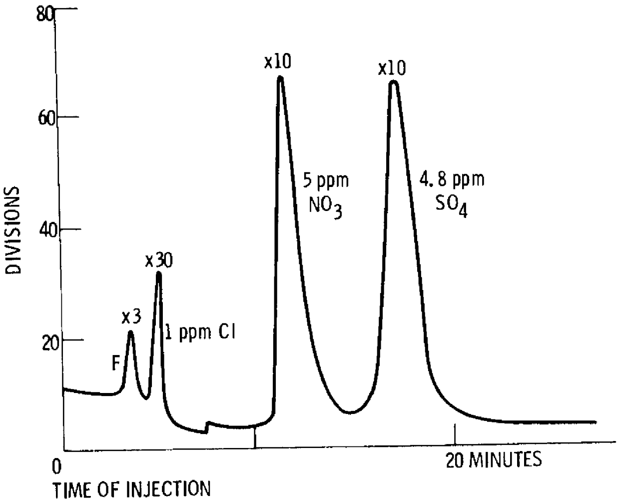

Figure 1. - Typical ion chromatogram.

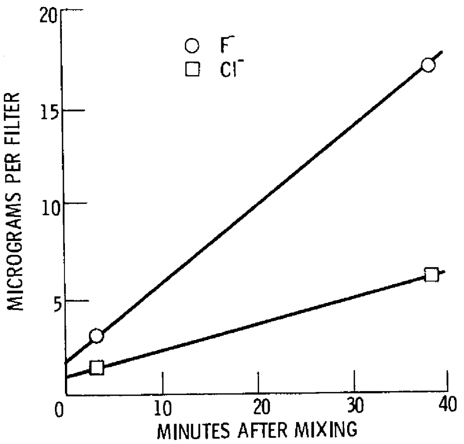

Figure 2. - Extrapolation procedure for the determination of F^- and Cl^- in the presence of dibutoxyethylphthalate.