Note

Correction for artifacts in the analysis of atmospheric aerosols

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The analysis of complex organic mixtures extracted from airborne particulate matter at the trace and ultra-trace levels requires analytical procedures which avoid the introduction of artifacts. However, contamination may arise from many sources: from materials and reagents, from sample handling before and after extraction, from glassware in contact with the sample, from the syringe at injection, or during sample storage. Introduction of contaminants when using various types of plastic tubing during sample condensation[1], and contamination by phthalates of intravenous solutions stored in poly(vinyl chloride) containers have been reported[2]. During a recent study involving analysis of organic and inorganic matter collected on cellulose filters by High Volume (Hi-Vol) filtration, it was discovered that the foil-lined screw-cap vials used for storage of extracted organics introduced artifacts into the methanol sample condensates[3]. Although cellulose filters were chosen for their low background levels of inorganic compounds, it has been reported that these filter elements contain high background levels of aliphatic hydrocarbons[4].

Very high levels of sample contaminants may not always necessitate discarding of samples which can not be repeated. A correction procedure can be used to obtain valid analyses free of artifacts. For chromatographic analysis of organic condensates, the retention indices of contaminant peaks can be used to identify their presence in samples, thus allowing corrections to be performed. A method is described using computer programs to calculate retention indices of chromatographic peaks and display detected components as peak area *versus* retention index bar-graph plots. Comparison of sample plots with plots of contaminants from various sources allows identification of these artifacts in the sample. Subtraction of contaminant peaks is done manually by the analyst. Plotting the sample data after subtraction of contaminant peaks will give a better representation of the organic material which originated from the original sample.

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EXPERIMENTAL

Instrumentation

Chromatographic analyses were performed using a Hewlett-Packard 5830A gas chromatograph (GC) equipped with flame ionization detector (FID) and a 1.8 m × 2 mm I.D. glass column packed with 100–120 mesh Aue Packing (AP)[5,6]. GC operating conditions were: initial temperature, 80°; time at initial temperature, 4 min; program rate, 4°/min; final temperature, 240°; time at final temperature, 30 min; injection port temperature, 240°; detector temperature, 240°; helium carrier gas flow-rate, 30 ml/min. A standard mixture of normal hydrocarbons was run periodically to enable calculation of retention indices.

Collection and extraction of particulate matter

Airborne particulates were collected using the Hi-Vol filtration technique as described by the Air Pollution Measurements Committee[7]. Whatman 41 filter elements, 8 × 10 in., were used due to their low background levels of inorganics. Organic material was extracted from the particulate matter with 200 ml of distilled in glass grade methanol (Burdick and Jackson Labs., Muskegon, Mich., U.S.A.) overnight in a Soxhlet extraction apparatus. Final sample volumes of 1.0 ml were obtained by rotary evaporation under aspirator vacuum. Details of the extraction and concentration steps have been previously described[8].

Computer analysis of data

The computer program RICALC was used to calculate Kovats retention indices. Bar-graph plots of GC peak areas *versus* retention indices were generated by the program GCPLOT. Both programs were written in the Fortran IV computer language to run on the University of Waterloo IBM 360/75 computer. Plotting was done by Calcomp plotter. Descriptions of these programs have been given previously[9]. Subtraction of contaminant peaks was done manually based on comparison of retention indices and the overall chromatographic pattern. All cap contaminant peaks, and filter contaminant peaks greater than 10,000 area counts which appeared in the sample chromatograms were removed from the sample, irregardless of the abundance detected in the sample extracts.

RESULTS AND DISCUSSION

Total GC–FID area counts for a sample is a good indicator of the amount of organics present, since area counts for a particular compound is directly related to amount in grams of that substance through its response factor. The average area counts per cubic meter is an estimate of the total organic loading from the air particulate matter sampled. In a previous study using glass fiber filters with low contamination background, this value averaged 690 area counts per cubic meter of air sampled for 42 aerosol samples taken from an industrial area, and 244 area counts per cubic meter for 36 samples from a rural area[8]. The 10 Hi-Vol samples examined in this study, taken in an industrial area, had average values of 900 counts/m³, even though the time of sampling was considered to be a low-pollution period, and visual examination of the filters before extraction indicated light loadings. From further study it became obvious

that the organic extracts from these filters were contaminated from both material originally present on the cellulose fibers and also from the screw caps of the sample vials used to store the extracts. Since the airborne particulate samples could not be replaced, it was necessary to extract as much reliable information from the contaminated samples as possible. A correction procedure was then devised to provide valid analytical data.

Fig. 1 illustrates the correction technique used. For comparison purposes between components of different samples run on the same GC column, Kovats retention indices are preferred over retention times. Retention indices calculated by the computer program RICALC for components detected by GC–FID of a Hi-Vol filter extract, a corresponding cellulose filter blank, and cap contaminants are plotted versus their peak areas by the program GCPLOT. By comparing retention indices of components in the different samples, artifacts introduced into the sample from cap contamination and the filter used for aerosol collection can be determined.
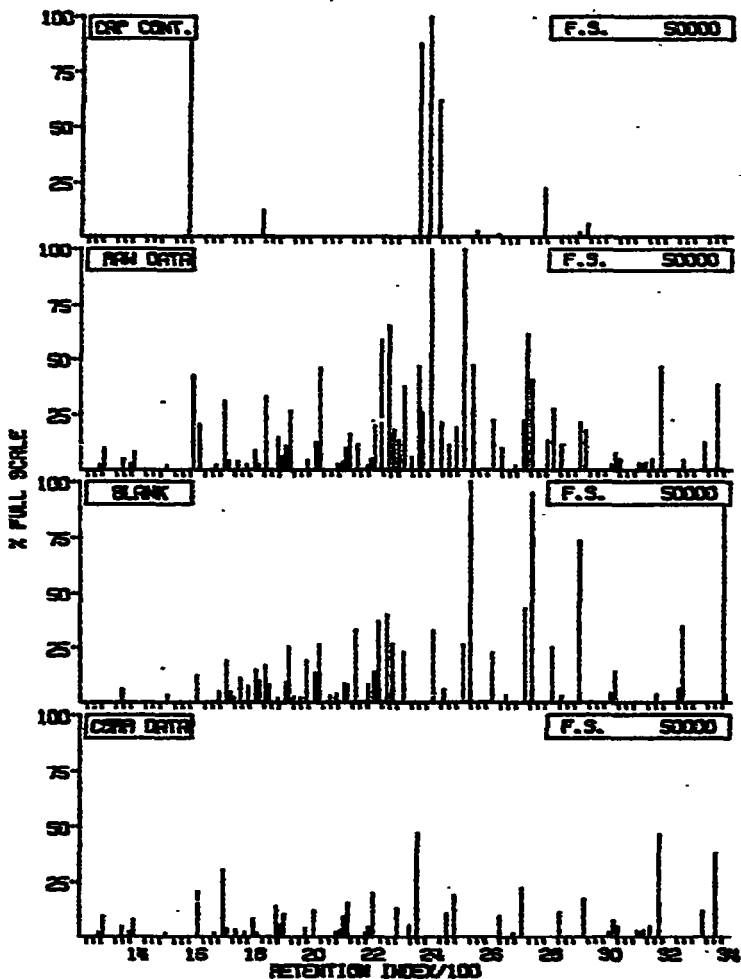

Fig. 1. GCPLOT comparison of detected contaminants with original and corrected data.

Fig. 1 also shows the plot of the corrected Hi-Vol sample, after subtraction of identified contaminant peaks. After contaminant subtraction, the average area counts for samples in this study was 388 counts/m³. A total of 17 major contaminant peaks originating from the blank filter were removed from the raw sample data. Since multiple blanks were not available to assess the consistency of concentration levels of the artifact peaks, corresponding sample peaks were completely removed from the raw data, even in cases when the sample peak was of much greater abundance. The average standard deviation between the retention indices of artifact peaks originating from the blank filter and corresponding peaks in the 10 sample extracts which were analyzed was 2.77 retention index (RI) units. The average standard deviation for RI values of identified cap contaminants was 5.09 RI units, although these artifacts were not difficult to identify in the raw sample chromatogram due to their distinctive pattern which is observed in Fig. 1. It is possible to automate the peak removal function, however the complexity of such samples makes close control over peak removal by the analyst desirable.

It can be seen in Fig. 1 that the filter blank contains a major peak at RI 3379 that is not present in the raw sample data. This peak could originate from another source of contamination than the filter paper used for aerosol collection. Also, there are several peaks present at higher levels in the blank than were detected on the sample filter. These differences could result from variable levels of contamination between filters, or from components being removed from the filter paper during sampling due to the large volumes of air being passed through the filter.

Although initial contamination levels were extremely high, and from two different sources, the use of Kovats retention indices and an effective means of visual comparison of several samples allowed most of the essential information to be extracted from the raw data. The usual procedure in such cases would be to discard the contaminated samples, however, this option is not desirable when replacement samples cannot be obtained. The resulting corrected data shown in Fig. 1 is a good estimate of the original composition of the aerosol sample before contamination. This procedure has also been used to determine very low levels of organic compounds on extracts from dichotomous filter elements[11]. A summary of the estimated contamination present from the cellulose filter used for aerosol collection from analysis of blank filter elements and from the sample storage vials used is given in Table I.

TABLE I

ESTIMATED AMOUNTS OF CONTAMINATION (AREA COUNTS) FOR SAMPLE SHOWN IN FIG. 1

	Hi-Vol sample
Total area	765317
Filter blank contamination	485561
Cap contamination	150022
Total percent contamination	83
Estimated organics from particulate matter	129734
Estimated organics per m³ of air sampled	164

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