very easily accomplished by rerunning one or both of these programs.

When a series of samples is injected and analyzed, all chromatograms thus generated are labeled with sample identifications, sizes, weights, volume injected, and attenuation used with yet another program. Then, the user is ready to invoke CAPPIS to analyze the data.

This analytical package consists of a menu from which the user chooses one of [currently] three options:

1) identify and quantitate pesticide residues with two or with three columns;
2) quantitate a multicomponent sample such as a PCB, chlordane, or toxaphene, when the identity of the sample has been established;
3) compare different multicomponent standards with a multicomponent sample to deduce its identity.

Essentially, the software sorts the peak data into various sets of arrays which are then manipulated according to which option is chosen. For the first option, it compares sample chromatograms with those of different pesticide standards analyzed the same day. Positive identifications are based upon retention time matches between all the columns used as long as the RT for each peak in question is within its specified window. After passing a peak height ratio test, a result is calculated; if it is above experimentally determined detection limits, it is printed on the report.

Since it is not practical to maintain any sort of "library" of PCB patterns (due to varying detector response, operating parameters and column characteristics between different instruments), option #3 functions as a useful tool in assigning an identification between similar PCBs (e.g., Ar1248 vs Ar1254). Once the identity of a particular PCD has been established, it is a simple matter to quantitate the results with option #2.

In contrast to the manual quantitation method, the sum of the peak heights from ALL the columns used is employed for computing results, not simply the peak height from the primary column. When quantitating a set of multicomponent samples versus a standard, CAPPIS adjusts itself to varying numbers of peaks, so that the maximum possible number of peak matches can be used in each case. This provides greater accuracy and reproducibility due to an error leveling effect.

The software is open-ended. By adding additional testing loops either internally or in the form of subroutines, further refinements, currently under study in our laboratory, can be made to option #3. Peak data arrays can be extended in various directions to encompass the use of three or more different standards and/or columns. Arrays could also be added to option #1 for additional testing loops such as relative retention time ratios for deducing possible identifications of pesticides not contained in the standards.

During the past several months that CAPPIS has been in routine use, a time savings of one man-hour per instrument per day has been realized. The software has been used to successfully pass proficiency tests at the federal and state levels. Additionally, it has provided a reliable method of tracking both instrument performance and quality control trends.

Sequential Automated Analysis System for Lower Oxygenated Organic Compounds in Ambient Air

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A completely automated system controlled by a microcomputer was developed for hourly analyses of lower oxygenated organic compounds (LO_x) in ambient air at the sub-ppb level. This system has some advantages, compared with manual procedures, including 1) good repeatability, 2) easy data processing, 3) easy accumulation of extensive data throughout the day and night, and 4) reduction of labor. Consecutive measurements using this system for 6–15 days have been carried out several times since November 1985 in Tokyo.

1. Introduction

LO_x are formed by the degradation of atmospheric hydrocarbons by free radicals, and are also emitted from various sources [1]. These compounds have been identified and measured in air [1–4], however, little is known about their concentration in the environment.

The accumulation of a large amount of data is essential for elucidation of the phenomena induced by the existence of LO_x. For this purpose, a practical and durable automated system was developed.

2. Experimental

2.1 Sampling Trap

Four kinds of adsorbents (Porapak–N, –Q, –T and Chromosorb 104) were examined for collection ability, and for desorption efficiency of LO_x and their parent compounds by heating. The results showed Chromosorb 104 (C104) to be superior to the other 3 adsorbents when a stainless steel tube (3 mm i.d. × 16 cm) packed with 0.4 g of C104 was used for the sampling tube. The collection volume of this trap for LO_x was estimated to be 2.4 L or more at 0 °C.

2.2 Sampling Air

An air sample was drawn at a height of 20 m from the ground and 3 m from the walls through a 20 m Teflon tube (6 mm o.d.) covered with a black tube. To reduce the loss of the compounds through the tube, the air sample was continuously drawn with a pump at a flow rate of 1 L/min. A portion of the air was sucked from the end of the main air stream for 30 min with a flow-controlled pump, through the sampling trap (kept at ca. 0 °C) using a flow rate of 45–50 mL/min to collect the LO_x in the air sample.

2.3 Chromatographic System

The system with an automated sampler is shown in figure 1. Two precolumns (BCEF and s.PQ in table 1) are used for the pre-fractionation of aliphatic hydrocarbons (AlHC) and aromatic hydrocarbons (ArHC), because some of AlHC overlap LO_x in chromatograms and ArHC prolong the analytical time.

The peaks in chromatograms of air samples were periodically identified by GC/MS. If the method requires sample sizes of more than 10 L, another sampling method was used [i.e., a trap (3 mm i.d. × 18 cm Teflon tube) packed with quartz wool impregnated with water was installed between 1.PQ and FID, with the LO_x peaks confirmed by their disappearance from the chromatograms].

The switching of the valves, fan, heater, cooler, GC, and data processor are controlled with a microcomputer and an interface. An air sample was ataken every hour for 30 min, and the chromatograms and the processed results were printed on chart paper and stored on floppy disks.

3. Results and Discussion

The reproducibility tests using a specially prepared gas containing LO_x at ppb levels showed that the overall system precision for LO_x was 1–5% (RSD) during one day, and the changes of the retention times were less than 0.5% (RSD). Detection limits with signal-to-noise of 4 were 0.5 ng for methanol, 0.1 ng for acetaldehyde and 0.1–0.5 ng for others. This corresponds to ca. 0.3 ppb of methanol and ca. 0.04 ppb of acetaldehyde respectively, in a 1.5 L air sample.

A typical chromatogram obtained with this system is illustrated in figure 2, showing the concentrations of some LO_x and ArHC species. Since the acetone and isopropanol peaks might contain other compounds, their values shown in figure 2 are considered to be tentative.

Table 1. Operating conditions for gas chromatograph

	Packings	Tube (SUS)	GC conditions
P1	N,N-bis(2-cyanoethyl) formamide [BCEF] on Chromosorb W (60/80)	3 mm (i.d.) 1.5 m (long)	Room temperature (18–30 °C) N_2 (38 mL/min)
P2	Porapak Q (50/80) [s.PQ]	2 mm (i.d.) 25 cm (long)	124 °C(12.5 min) – 4 °C/min(15 min) – 184 °C(25 min) N_2 (41 mL/min)
AC	Porapak Q (80/100) [1.PQ]	1.5 mm (i.d.) 4 m (long)	38.25 °C – 1.5 °C/min(14.5 min) – 20 °C/min(2.5 min) – 10 °C/min(3 min) – 2 °C/min(20 min) – 180 °C(13 min) N_2 (33 mL/min)

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The monitoring of LO_x for 6–15 days has been carried out several times in the metropolitan area of Tokyo since November 1985, and data on more than 1800 samples have been obtained. Acetaldehyde, C_1-C_3 alcohols, and acetone were constantly observed in chromatograms. Acrolein, C_2-C_3 esters, propionaldehyde, C_4-C_5 ethers, and methylethylketone were occasionally detected. This system has worked satisfactorily for more than 2500 hours without any exchange of parts in the devices, and has proved to be practical and durable.

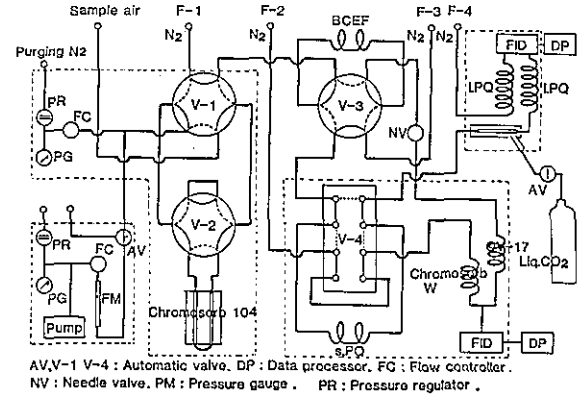

Figure 1. Schematic for automated sampling and analysis.

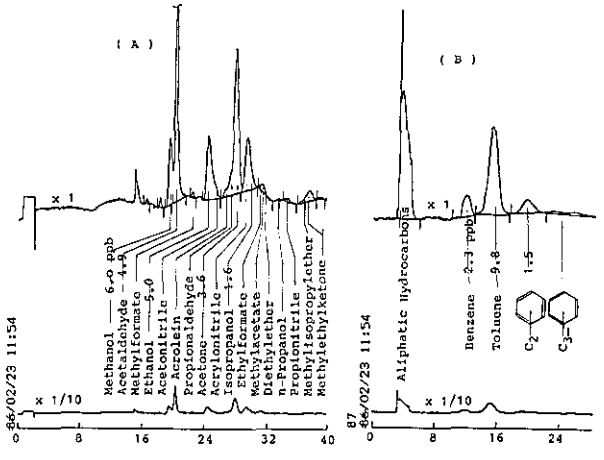

Figure 2. Gas chromatograms of ambient air (1.38 L).

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Trace Level Quantitation of Phenyltin Compounds Using HPTLC

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We sought to develop a rapid analytical technique for the determination of triphenyltin pesticide residues in food. HPTLC offers such an approach since it is rapid, selective, sensitive and has a high throughput [1]. The quantitative aspects of HPTLC have been documented and reviewed [2]. Conventional TLC has been used to separate butyltin compounds, subsequently detected using chemical oxidation and colorimetry of the pyrocatechol-complex [3]. TLC has also been used to speciate organotin compounds that were detected by anodic stripping voltammetry [4]. A study of the mammalian metabolism of organotins used normal and two-dimensional TLC, followed by photolysis and treatment with visualizing reagents (8-hydroxy-5-sulfonic acid, pyrocatechol violet, or dithizone) to identify the chromatographic components