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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.

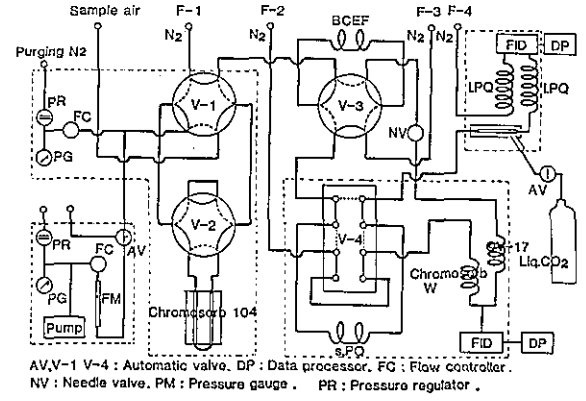

Figure 1. Schematic for automated sampling and analysis.

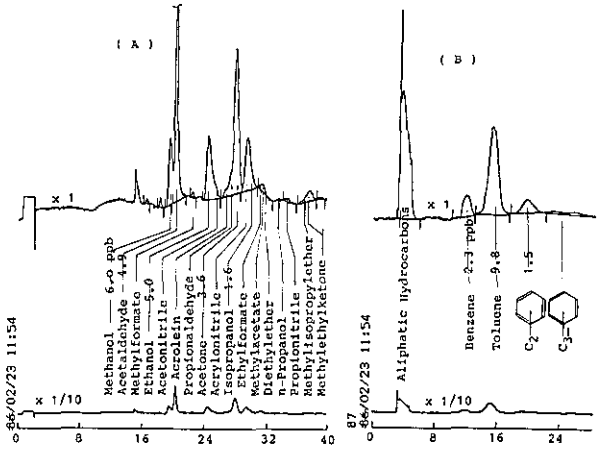

Figure 2. Gas chromatograms of ambient air (1.38 L).

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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

[5]. Another TLC method for organotins reported retention factor values for a series of tri-, di- and monosubstituted organotins; hematooxylin was used for visualization and the good resolving capacity of TLC was demonstrated [6]. HPTLC quantitation of butyltins in a wood extract matrix has been reported using post-development photolysis and colorimetric detection by complexation with pyrocatechol violet [7]. When complexed with inorganic tin and some organotins, morin produced a fluorescent complex; this principle forms the basis of this sensitive (DTL: 10^{-7} to 10^{-9} M) and selective analytical method [8].

The present study examines the use of HPTLC with in situ post-development derivatization using morin; fluorescence detection in HPTLC typically offers greater sensitivity and selectivity than other light absorption methods [9]. Fluorescence enhancement plate coatings are an important aspect of HPTLC quantitative analysis because they produce enhanced and stabilized fluorescence on HPTLC plates [16,17].

Mixtures of tetraphenyltin (TTPT), triphenyltin chloride (TPTCl), diphenyltin dichloride ($DPTCl_2$), and monophenyltin trichloride ($MPTCl_3$) were resolved using high performance thin layer chromotography on silica gel with retention factor values of 0.80, 0.35, 0.20, 0.01, respectively. Inorganic tin impurities were strongly adsorbed and did not migrate from the origin. Diphenyltin dichloride, monophenyltin trichloride, and inorganic tin components reacted with morin to produce fluorescent complexes. Post-development exposure of the plate to ultraviolet light photodegraded the organic components which, after morin treatment, exhibited greater fluorescence than the organotins. This photolysis technique permitted the visualization of the otherwise nonfluorescent tetraphenyltin and weakly fluorescent triphenyltin spots.

The components were quantitated using scanning densitometry. The working range varied from a maximum of 222 nanograms to a minimum of 1 nanogram, depending on the particular component and the excitation wavelength chosen. Thirty standards, each containing five components, were spotted, developed, derivatized, and scanned at least three times to produce 480 pieces of data within 4 hours. Calibration curves showed an instrumental error of 1.5% relative standard deviation, and a spotter and intraplate variation of 9.0% relative standard deviation. The inherent multiplicity of high performance thin layer chromatography allows for multiple sampling and analysis, thereby yielding significantly increased precision and high sample throughput. The chromatography and detection of butyltins and cyclohexyltins were also examined.

The four chromatograms in figure 1 demonstrate the HPTLC of the compounds TTPT, TPTCl, $DPTCl_2$, $MPTCl_3$, and organic tin on silica gel using two different mobile phases, with and without the use of photolysis prior to morin derivatization and fluorescence detection. Chromatograms 1a and 1b used mobile phase A (5% acetic acid, 20% methylene chloride, 75% isooctane v/v) which completely resolves the organotins. However, $MPTCl_3$ is not moved from the origin and if inorganic tin compounds are also present $MPTCl_3$ is not resolved from them, therefore a stronger mobile phase in a separate development is required to resolve $MPTCl_3$ from inorganic tin. The efficiency is excellent with no tailing or peak asymmetry. Photolysis increases the fluorescence of each compound, and is critical for the detection of TTPT, and TPTCl. Chromatograms 1c and 1d use a stronger mobile phase B (30% acetic acid, 70% chloroform v/v). The Rf values of TTPT, TPTCl, $DPTCl_2$, and $MPTCl_3$ were: 0.85, 0.55, 0.25, and 0.00 using mobile phase A; and 0.65, 0.56, 0.14, and 0.05 using mobile phase B. TPTCl, triphenyltin hydroxide (TPTOH), and triphenyltin acetate (TPTAc) all elute as TPTAc, as established using preparative TLC and FT-IR comparisons.

The calibration curves shown in figure 2 are for $MTPCl_3$, $DPTCl_2$, TPTCl, and TTPT with the analyte-morin complex excited at 313 nm. The error bars at each measured concentration level indicate the mean value, plus and minus one standard deviation ($N=6$). The relative slope of each line correlates qualitatively to the percent of tin in each molecule; thus the detection limit is lowest for $MPTCl_3$.

Figure 3 shows 15 chromatograms from authentic organotin reference compounds that were applied to a single 10-cm × 10-cm HPTLC plate, and analyzed by the described method. The organotin samples and the corresponding peaks were: fenbutatin oxide (samples 1–3; peak A); triphenyltin oxide, TPTO (samples 4–6; peak B); monocyclohexyltin tribromide, $MCyTBr_3$ (samples 7–9; peak C); dicyclohexyltin dibromide, $DCyTBr_2$ (samples 7–9; peak D); tricyclohexyltin bromide, TCyTBr (samples 7–9; peak E); monobutyltin trichloride, $MBTCl_3$ (samples 10–12; peak F); dibutyltin dichloride (samples 10–12; peak G);

tributyltin chloride, TBTCl (samples 10–12; peak H); monophenyltin trichloride, $MPTCl_3$ (samples 13–15; peak I); diphenyltin dichloride, $DPTCl_2$ (samples 13–15; peak J); triphenyltin chloride (samples 13–15; peak K); tetraphenyltin, TTPT (samples 13–15; peak L). Each standard had an approximate mass of 10 ng except the $MBTCl_3$, and $MPTCl_3$ which were of uncertain quantity. The standards were eluted with mobile phase A to a 5-cm solvent front. The processed plate was scanned longitudinally with 15 4-cm passes to measure the fluorescence emitted at 515 nm (broad band pass filter) using 436 nm excitation. The results in figure 3 demonstrate that resolution of organotins between classes of compounds is excellent (i.e., R_4Sn, R_3SnX, R_2SnX_2, and $RSnX_3$ where R = alkyl or aryl groups).

Currently work is being done to incorporate this determinative step to quantitate TPT residues in potatoes. Quantitation of TPT at 0.1 ppm has been accomplished. Potato extracts have been screened for TPT down to 0.01 ppm. This determinative method has also been used to measure tri-, di-, and monobutyltin chloride in water down to 0.01 ppm.

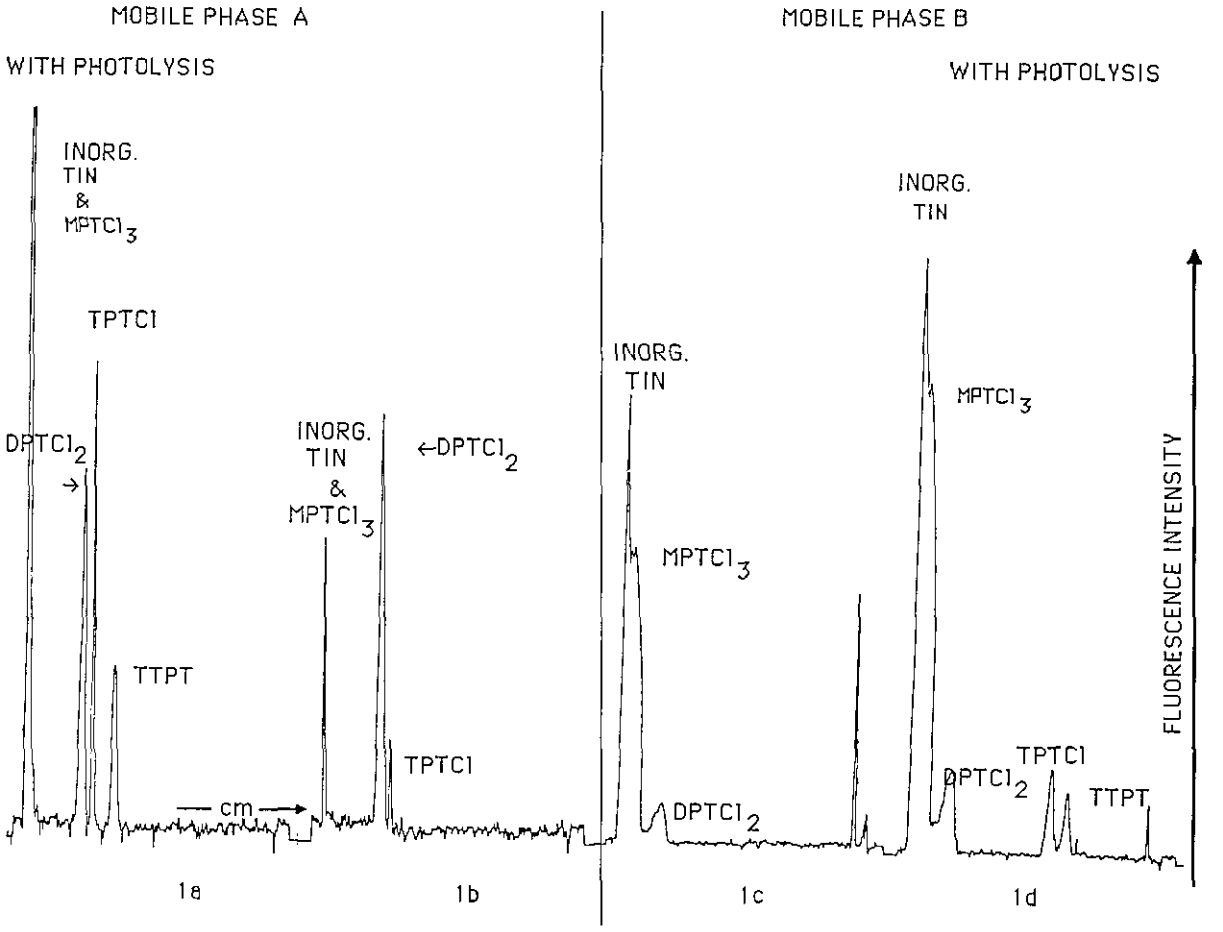

Figure 1. Four chromatograms separating inorganic tin, $MPTCl_3$, $DPTCl_2$, TPTCl, and TTPT. Chromatograms 1a and 1b used mobile phase A, and 1c and 1d used mobile phase B.

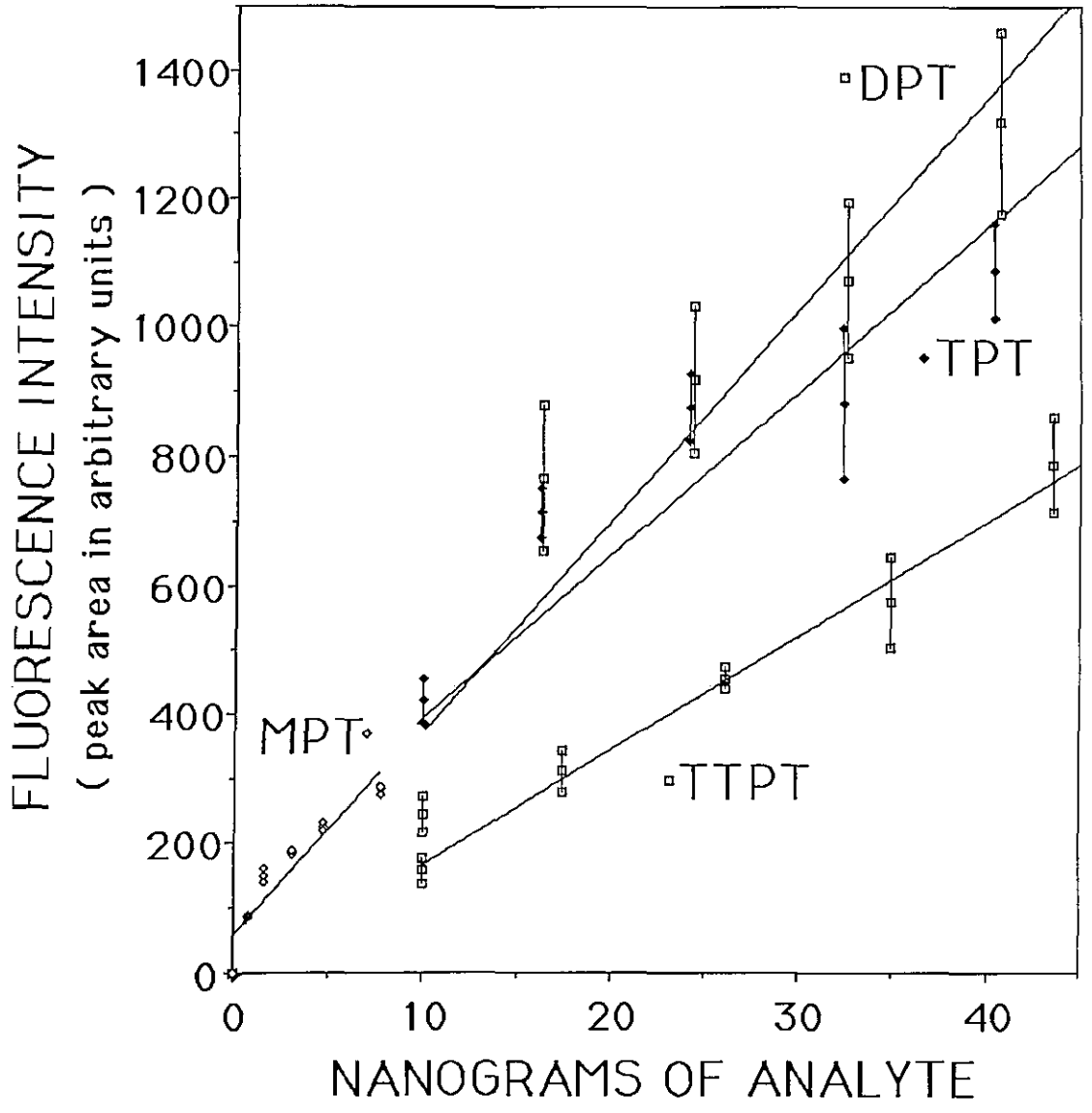

Figure 2. Fluorescence calibration curves for $MPTCl_3$, $DPTCl_2$, TPTCl, and TTPT excited at 313 nm. Error bars show ±SD.

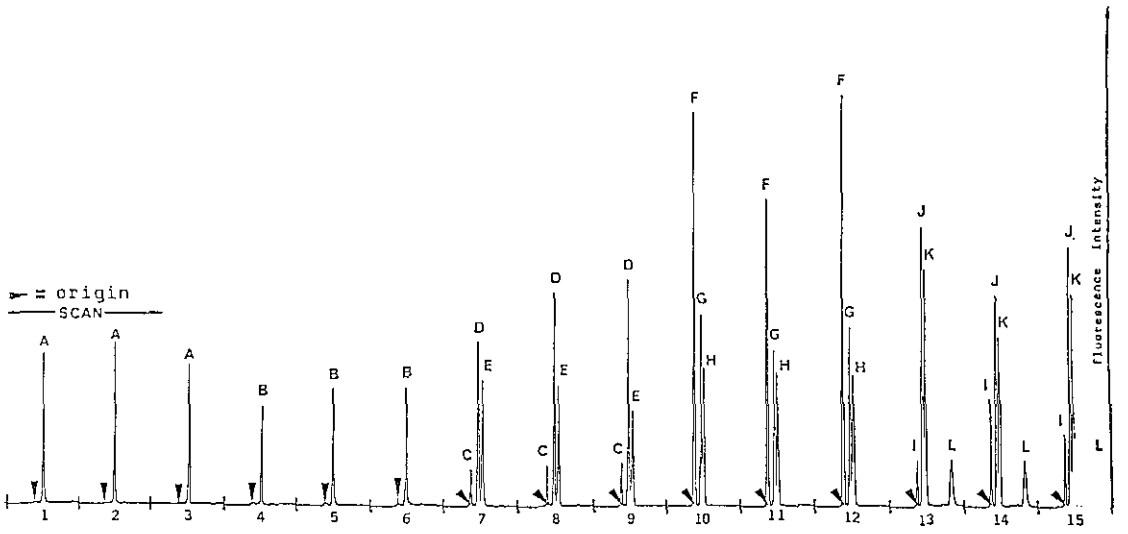

Figure 3. Fifteen chromatograms produced from 4 cm longitudinal densitometer scans across a 10 cm×10 cm HPTLC plate with 15 organotin samples. Components: A, 6 ng fenbutatin oxide; B, 7 ng TPTO; C, $MCyTBr_3$; D, 11 ng $DCyTBr_2$; E, 11 ng TCyTBr; F, 11 ng $MBTCl_3$; G, 11 ng $DBTCl_2$; H, 13 ng TBTCl; I, $MPTCl_3$; J, 12 ng $DPTCl_2$; K, 12 ng TPTCl; L, 13 ng TTPT.

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Determination of Chromium(III) and Chromium(VI) by Ammonium Pyrrolidine Dithiocarbamate-Methyl Isobutyl Ketone-Furnace Atomic Absorption Spectrometry

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The determination of Cr(III) and Cr(VI) in environmental and biological systems is of interest because the toxicity of this metal depends on its oxidation state. Cr(III) is essential to mammals, while Cr(VI) is toxic. In addition to its existence in the two main oxidation states of +3 and +6, Cr occurs in the aquatic environment at $\leqslant$ ng/mL levels. Therefore, some form of preliminary separation and preconcentration is required to determine the low levels of individual Cr species by sensitive analytical techniques, such as graphite furnace atomic absorption spectrometry (GFAAS) [1,2].