Trace Analysis for Polycyclic Aromatic Hydrocarbons (PAH) Using Capillary GC with Photoionization Detection

by

James E. Arnold

National Institute for Occupational Safety and Health
Division of Physical Sciences and Engineering
Methods Research Branch
Organic Methods Development Section

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Abstract

A GC technique using a fused silica capillary column and a photoionization detector (PID) equipped with an 8.3 electron-volt lamp was studied. The goal was to develop a rapid instrumental technique for detection of polycyclic aromatic hydrocarbons (PAH) in road asphalt and diesel engine emissions. With the 8.3 electron-volt lamp, 50-μL injections were found to be practical. Lowest detectable levels for 5 PAH were lower than with use of a 10.2 electron-volt lamp and flame ionization detector. For 3 PAH at a given level, better precision of measurement was obtained using the GC-PID compared with a liquid chromatography technique. In preparation of solutions, simple filtration was adequate before injection into the GC in view of minor benefit shown by lengthly, sample fractionation. Aliquots containing an estimated 20 μg or less of road asphalt or diesel emissions are recommended for injection into the GC. With a run time of 14 minutes, the GC-PID may be used to analyze for EPA's 16-priority pollutant PAH.

INTRODUCTION

A photoionization detector has become a useful addition to the list of gas chromatography detectors (1,2). It houses an ultraviolet lamp of a specified electron-volt rating. Molecules with ionization potentials below the lamp energy are detected(3). Polycyclic aromatic hydrocarbons (PAH) have distinctly low ionization potentials, below 8.3 electron-volts. Thus, an ultraviolet lamp with greater than or equal to 8.3 electron-volts may be used to detect PAH. Other analysts have used a 10.2 electron-volt lamp for trace level determination of PAH in cigarette smoke(4), fly ash particulates, coke oven gases, and other combustion effluents(1). With the 10.2 electron-volt lamp, the sensitivity was increased 40 ^{o}/o for five aromatic compounds using argon as carrier gas in place of nitrogen(2). Further improvement of the photoionization detector now allows operation at 300 ^{o}C which permits determination of higher molecular weight PAH.

A photoionization detector with a low energy 8.3 electron-volt lamp was used for this research. It held expectation for avoiding detection of sample components with ionization potentials greater than 8.3 electron-volts. Use of a high resolution, capillary column with the photoionization detector was proposed to be specific enough for PAH to negate any need to fractionate samples. To arrive at a suitable PAH fraction for analysis, carbon blacks and related substances often require lengthly cleanup procedures(5). Without sample cleanup, the GC-PID technique was intended to provide better precision, higher sample throughput and acceptable lowest detectable levels in view of an in-house liquid chromatography method (Table II, Note (a)). Its unacceptable precision and long analysis time presented the need for an improved instrumental technique. The instrumental conditions that emerged for the GC-PID were applied to analysis of solutions of road asphalt, an extract of particulate diesel emissions and fractions of the extract. With these solutions, the GC-PID was evaluated to define its usefulness in monitoring for hazardous PAH.

EXPERIMENTAL SECTION

Apparatus. A photoionization detector, PID (hnu Systems, Inc., Newton, Ma.) was positioned directly above the oven of a Varian 3700 gas chromatograph. For the PID, an 8.3 electron-volt, ultraviolet lamp was selected. It was operated at full intensity (9.4 on the dial) for maximum sensitivity. Continuous usage of the PID for longer than 1 week sometimes required re-tightening of screws in it to maintain performance. A 30-meter fused silica capillary column with non-extractable (DB-5) bonded phase, 1 ^{o}/o vinyl, 5 ^{o}/o phenylmethyl polysiloxane, was used. The column has a 0.32 mm i.d. and a 0.25 μm film thickness (J. and W. Scientific Inc., Rancho Cordova, CA.). The column entered a standard capillary injector-splitter system fitted with a baffle-type glass insert and spring. For minimal dead volume, the column was positioned flush with the split tip in the injector assembly and fully inserted into the detector. To control the septum purge, a valve was attached at the end of the purge line. Manual injections were made with 10-, 25-, and 100-μL syringes. Chromatograph detector signals were processed by a Hewlett Packard 3350 laboratory data system. Quantitation using peak heights rather than peak areas was found to give better precision.

Materials. Helium was used exclusively as the carrier gas. For increased drift velocity of photo-induced electrons in the photoionization detector, argon was used as the make-up gas. Both gases were passed through water and oxygen scavengers. A standard containing 16 PAH on EPA's list of priority pollutants was obtained from Supelco, Inc. This standard served as a model in selecting suitable gas chromatographic conditions for analysis of PAH in methylene chloride. To aid in determination of lowest detectable levels, a 5 component standard was used containing pyrene, benzo[b]fluorene, benz[a]anthracene, benzo[a]pyrene, and dibenz[a,h]anthracene. Pyrene and benzo[a]pyrene were obtained from Eastman Kodak Co.; benzo[b]fluorene, and benz[a]anthracene were obtained from Aldrich Chemical Co., Inc.; and, dibenz[a,h]anthracene was obtained from Pfaltz and Bauer, Inc. Methylene chloride (distilled-in-glass, analytical grade, Burdick and Jackson Laboratories, Inc.) was used for preparation of solutions.

PREPARATION OF SOLUTIONS FOR INJECTION INTO GC. The bulk road asphalt sample represented initially pre-heated material that was sprayed onto a road surface. To 261 mg of road asphalt, methylene chloride was added to give a concentration of 26.1 mg/mL. A 2-mL aliquot was placed in a 4-mL vial, and with the aid of a centrifuge, the solution was passed through a 0.45 μm nylon-66 filter (Rainin Instrument Co., Inc.) into another 4-mL vial. The two glass vials were joined by a dual, screw cap. In another vial, an aliquot of the filtered solution was added to methylene chloride to give a concentration of 1.2 mg/mL. A 50-μl aliquot of this solution was injected into the GC (Figure I).

Particulate diesel emissions in 7776 L of engine exhaust were collected on a glass fiber filter. The filter was then subjected to soxhlet extraction for 6 hours using 300 mL of methylene chloride. The extract was passed through a 0.5 μm Millipore FH filter, and with the aid of a rotary evaporator, the volume was reduced to 2 mL. During extraction, 47 mg was removed from the filter which gave the 2-mL extract a concentration of 23.5 mg/mL. A 2-μL aliquot of the concentrated extract was injected into the GC (Figure II).

A 200-μL aliquot from the 2-mL concentrated extract was fractionated according to a liquid chromatography procedure(6). The eight fractions were evaporated to dryness and the residues were dissolved in 0.5 mL of methylene chloride or tetrahydrofuran. Each fraction was analyzed for PAH on EPA's list of 16-priority pollutants using the GC-PID.

Gas Chromatographic Conditions. An initial oven temperature of 150 °C with a 3-minute delay was followed by a 25 °C/minute rise to 325 °C and held for 4 minutes. The injection port and photoionization detector temperatures were 240 °C and 300 °C, respectively. For detection of higher molecular weight PAH than benzo[ghi]perylene, the upper oven temperature, 325 °C was held for longer than 4 minutes. This was necessary, also, to recover from poorly resolved materials which were not totally eluted after 14 minutes. Excessive overloading of the column was avoided by injecting only slightly colored and filtered solutions of road asphalt and diesel exhaust.

The splitter vent remained closed throughout with these GC conditions. Volumes from 1 to 50 μL were injected with a septum purge flow-rate of 38 mL/minute helium. This flow rate was particularly needed with 50-μL injections to give minimal solvent tailing. Injections of 5 μL may be made with the septum purge off without excessive solvent tailing. The syringe needle remained in the injector assembly, fitted with a baffle-type glass insert, for 3 minutes to avoid sample loss at the septum. Due to back pressure, the plunger of the 100-μL syringe sometimes required holding down momentarily. Septa were not used more than 8 times especially with the 100-μL syringe.

The column pressure at the beginning of a run was 3.46×10^3 pascals. This pressure includes a linear velocity for helium through the column of 38.5 cm/sec. The combined flow rate of the column (2.1 mL/minute helium) and the make-up gas (27.5 mL/minute argon) was monitored at the PID exhaust port. Choice of column and detector are discussed below.

RESULTS AND DISCUSSION

A capillary column of suitable length for PAH analysis was selected using a 5-component standard containing pyrene, benzo[b]fluorene, benz[a]anthracene, benzo[a]pyrene and dibenz[a,h]anthracene. Injections of the standard were made onto a 15-meter glass capillary column and 10.7-, 15-, 30-, and 45-meter fused silica capillary columns. These were coated with 1 ^{o}/o vinyl, 5 ^{o}/o phenylmethyl polysiloxane known as SE-54, or an equivalent phase, DB-5, for the 30-meter column. The 30-meter non-extractable, DB-5 phase, fused silica capillary column was selected. It provided best sensitivity for the 5-PAH in the standard with sufficient resolution to allow for naphthalene. Naphthalene was the first PAH to elute of the 16 PAH on EPA's list of priority pollutants. PAH are readily soluble in methylene chloride with which the DB-5 phase showed no deterioration after 3 months.

A photoionization detector with an 8.3 electron-volt, ultraviolet lamp was selected, not only for its selectivity for PAH, but also for its low response to methylene chloride. With an ionization potential of 11.35 electron-volts, methylene chloride is not photoionized by the lower energy 8.3 electron-volt lamp to produce a positive detector response, but instead gave a negative response. The negative detector response to 50 μL of methylene chloride was completed well before early eluting PAH. With the PID with 10.2 electron-volt lamp or the flame ionization detector, responses to only 3 μL of methylene chloride affected measurement of early eluting PAH. Another shortcoming with use of a flame ionization detector was baseline rise during temperature programming of a 15-meter, SE-54 coated, glass capillary column. Both the 10.2 electron-volt lamp and flame ionization detector gave response to trace impurities in the solvent. Use of the 8.3 electron-volt lamp was, thus, favored with larger injections (up to 50 μL) as shown in Figure III.

Figure III shows a chromatogram of EPA's 16-priority pollutant PAH using optimal GC conditions. To avoid overloading of the column with methylene chloride from large injection volumes (>5μL), a septum purge flow rate of 38 mL/minute helium was necessary. Septum purge flow rates lower than 38 mL/minute gave excessive solvent tailing and decreased sensitivity with unacceptable precision. A baffle-type glass insert in the injector assembly was also necessary. It aided efficient transfer of PAH in large injection volumes, onto the front of the column. With a direct (or open)-type glass insert, methylene chloride emerged over most of the run, prohibiting PAH measurement.

An oven temperature program was selected to give maximum sensitivity for EPA's 16-priority PAH. For each PAH in the 5-component standard used above, initial oven temperatures of 110 ^{o}C and lower produced two peaks. An initial oven temperature of 150 ^{o}C was the highest temperature with which a 3-minute delay allowed naphthalene in a 50-μL injection to elute free of interference from methylene chloride. Temperature programming rates lower than 25 ^{o}C/minute caused the calibration curves to be convex, especially for dibenz[a,h]anthracene. To attain usable, quantifiable ranges for all of EPA's 16-priority PAH, raising the column to 325 ^{o}C was necessary.

Argon gave enchanced peak areas over helium as the make-up gas. Using the 10.2 electron-volt lamp, peak areas increased 20 ^{o}/o for pyrene, 22 ^{o}/o for benzo[b]fluorene, 34 ^{o}/o for benz[a]anthracene, 38 ^{o}/o for benzo[a]pyrene and 33 ^{o}/o for dibenz[a,h]anthracene. Susceptibility of the ultraviolet lamp window to pentration by helium above 250 ^{o}C gave argon further preferrence as make-up gas. No lamp problem was noted with use of helium as carrier gas and argon as make-up gas with the photoionization detector at 300 ^{o}C.

Lowest detectable levels were similar whether the splitter vent opened at 0.5 minute after an injection or remained closed during the entire run for injection volumes up to 8 μL. Larger than 8 μL injections with the condition that the splitter open at 0.5 minute, gave unacceptable precision. By keeping the splitter vent closed throughout the run, the precision of measurement did not significantly change for injection volumes of 3 to 50 μL.

Figure IV shows a 50-μL injection containing 1.8-ng pyrene, 2.0-ng benzo[b]fluorene, 1.6-ng benz[a]anthracene, 2.0-ng benzo[a]pyrene and 3.8-ng dibenz[a,h]anthracene. At these levels, relative standard deviations ranged from 12 ^{o}/o to 23 ^{o}/o for four injections. Lowest detectable levels were estimated from these data to be 1.0-ng injected for each PAH. At the 1.0-ng level, peak heights would be aproximately 3 times the baseline noise variability of 1-mm (0.01 mV). Lowest detectable levels were proportionally higher with 20- and 3-μL injections. The gain using 50-μL injections with the GC-PID with 8.3 electron-volt lamp emerged in comparision of lowest detectable levels with a 10.2 electron-volt lamp, flame ionization detector and a liquid chromatography technique (Table II).

Lowest detectable levels given in Table II represent peak heights approximately three times the baseline noise variability. With the GC-PID with 8.3 electron-volt lamp, lowest detectable levels were 5 to 40 and 5 to 150 times lower than with use of the 10.2 electron-volt lamp and flame ionization detector, respectively. The 10.2 electron-volt lamp gave 1 to 3.8 times lower detectable levels than the flame ionization detector. Other researchers noted, however, at least 10 to 40 times better sensitivity with the 10.2 electron-volt lamp than with flame ionization detection(7). With either detector, lowest detectable levels by the in-house liquid chromatography method (Table II), were not reached. Use of the GC-PID with 8.3 electron-volt lamp came closest with 4 to 30 times less sensitivity than the liquid chromatography method for 5 PAH (Table II).

The air sampling device used for the liquid chromatography method in Table II consisted of a glass fiber filter backed by primary and backup beds of Tenax-GC. The sampling stages were extracted with acetonitrile and aliquots were analyzed by reverse-phase high-pressure liquid chromatography with fluorescence detection. Injections of 25 μL were made onto a Vydac 201TP column. By this liquid chromatography method, relative standard deviations were higher, however, at the 0.2 μg/mL level for pyrene and benz[a]anthracene than with use of the GC-PID with 8.3 electron-volt lamp (Table III). An analysis using the liquid chromatography method took 65 minutes, but with use of the GC-PID, only 20 minutes was necessary between injections of standards. These standards had a variability of retention time of 0.02 minutes. Next, using the GC-PID with 8.3 electron-volt lamp, solutions containing road asphalt and extracts of particulate diesel emissons were injected.

Figure I shows a 50-μL injection of a filtered solution containing 1.2 mg/mL road asphalt in methylene chloride. The raised baseline following passage of the solvent in Figure I was due to column overloading. Thus, injection of a more concentrated solution of road asphalt was not practical. Using retention time as a basis of identification, fluoranthene, pyrene and chrysene were found in the road asphalt. However, seven additional PAH were found in the road asphalt by a liquid chromatography technique (Table IV). For this technique, an aliquot of filtered road asphalt in cyclohexane was evaporated to dryness and the residue dissolved in acetonitrile. An aliquot was then injected onto a Supelco LC-PAH column and eluted with a programmed gradient of acetonitrile and water. The column effluent was monitored for PAH using a fluorescence detector with excitation at 340 nm and emission at 425 nm. With this liquid chromatography technique, concentrations for PAH in road asphalt (Table IV) were 1.2 to 11 times below estimated lowest detectable levels with use of the GC-PID with 8.3 electron-volt lamp.

To improve the sensitivity with use of the GC-PID, reduction of major consituents in a solution of road asphalt was attempted with use of silica gel. One milliliter of 1.2 mg/mL road asphalt in methylene chloride was shaken with approximately 100 mg of 200-mesh silica gel. Analysis of the solution gave a chromatogram unchanged from before treatment with silica gel. Similarly, major constituents in road asphalt were not sufficiently reduced with use of a Waters silica gel cartridge. This cartridge was also found to elute a persistent contaminant even after rinsing it with 40 mL of methylene chloride.

Figure II shows a 2-μL injection of a concentrated, methylene chloride extract of particulate diesel emissions. As with the road asphalt, the unresolved, major constituents in the diesel exhaust extract were not totally eluted in 14 minutes. Thus, the quantities injected, approximately 60-μg road asphalt and 47-μg extracted diesel emissions, were excessive for routine analysis using the GC-PID with 8.3 electron-volt lamp. The maximum quantities injectable for routine analysis were estimated to be 20-μg road asphalt and 15-μg extracted diesel emissions. For a 15-μg injection of extracted diesel emissions, sufficient sensitivity would have remained to detect fluoranthene and pyrene as found. In search of additional PAH, an aliquot of the extract was fractionated by a liquid chromatography procedure(6). The eight fractions were evaporated to dryness and the residues were each dissolved in 0.5-mL of methylene chloride or tetrahydrofuran. For maximum sensitivity for PAH, 50-μL aliquots from the fractions were analyzed using the GC-PID with 8.3 electron-volt lamp. In addition to fluoranthene and pyrene, only chrysene and benzo[b]fluoranthene or benzo[k]fluoranthene were detected in any of the fractions. Concentrations found for fluoranthene and pyrene in the extract (Figure II) were 5.1 and 4.4 μg/mL, respectively.

The calibration curve for pyrene (Figure V) was typical of detector response at low levels to the 5 PAH in Figure IV. A quadratic equation was used to generate the curve from 0 to 0.29 μg/mL pyrene in methylene chloride. Each point in the plot represents the average of four injections. At the lowest level injected (0.036 μg/mL), the relative standard deviation for pyrene was 18.2 ^{o}/o.

CONCLUSIONS AND RECOMMENDATIONS

Use of 50-μL injections was found to be practical for best sensitivity using the GC-PID with 8.3 electron-volt lamp. For 3 PAH at a given level, better precision of measurement was obtained using the GC-PID compared with a liquid chromatography technique. Lowest detectable levels for 5 PAH were lower than with use of a 10.2 electron-volt lamp and a flame ionization detector. In preparation of solutions, simple filtration was adequate before injection into the GC. Aliquots containing an estimated 20 μg or less of road asphalt or diesel emissions are recommended for injection into the GC. While not as sensitive as liquid chromatography with fluorescence detection, the GC-PID technique is useful in analysis for EPA's 16-priority pollutant PAH.

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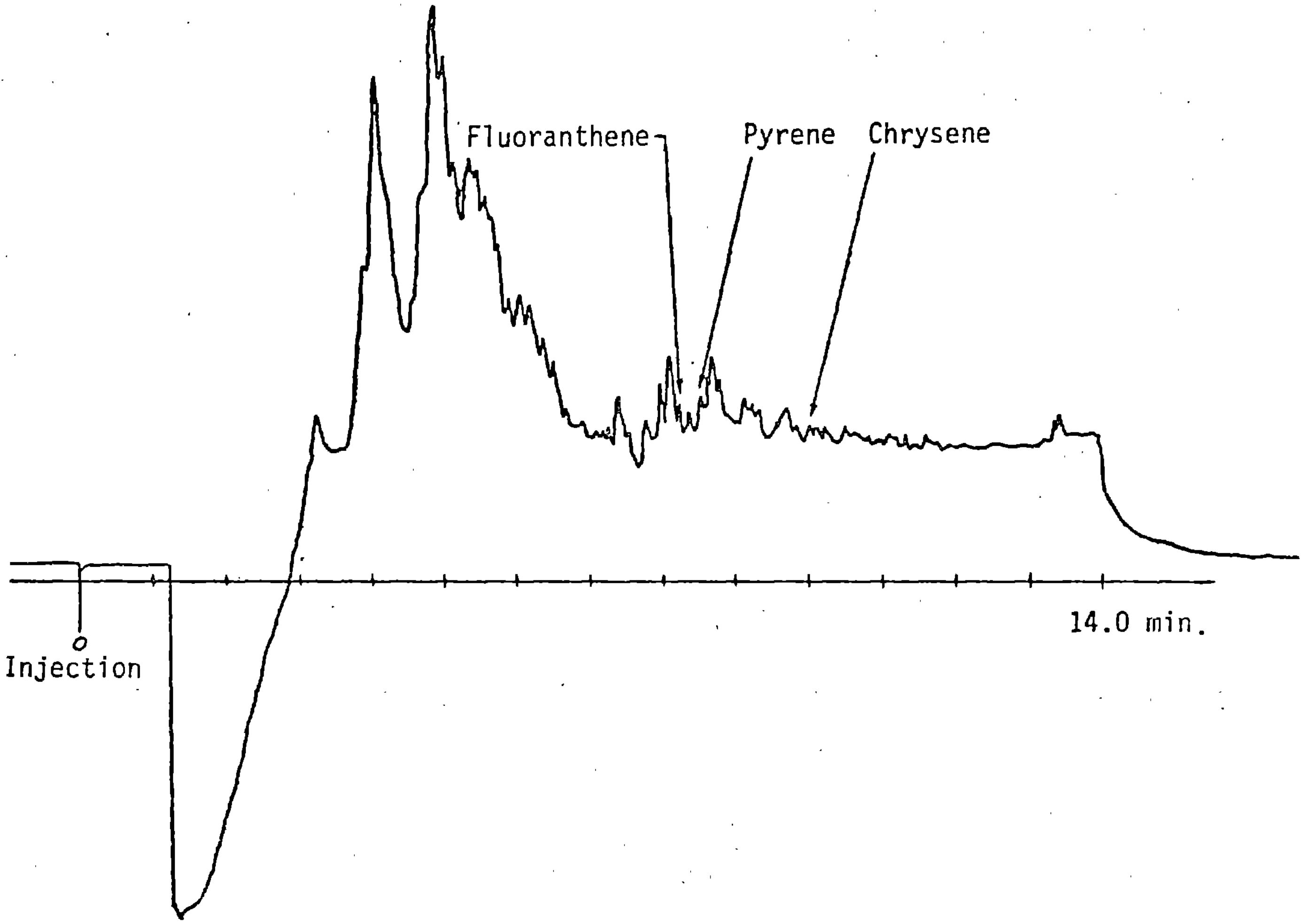

Figure I. Chromatogram of a 50-μL injection of 1.2 mg/mL filtered road asphalt in methylene chloride. A GC-PID with an 8.3 electron-volt lamp and a 30-meter, DB-5 phase, fused silica capillary column were used. An initial oven temperature of 150 °C with a 3-minute delay was followed by a 25 °C/minute rise to 325 °C and held for 4 minutes.

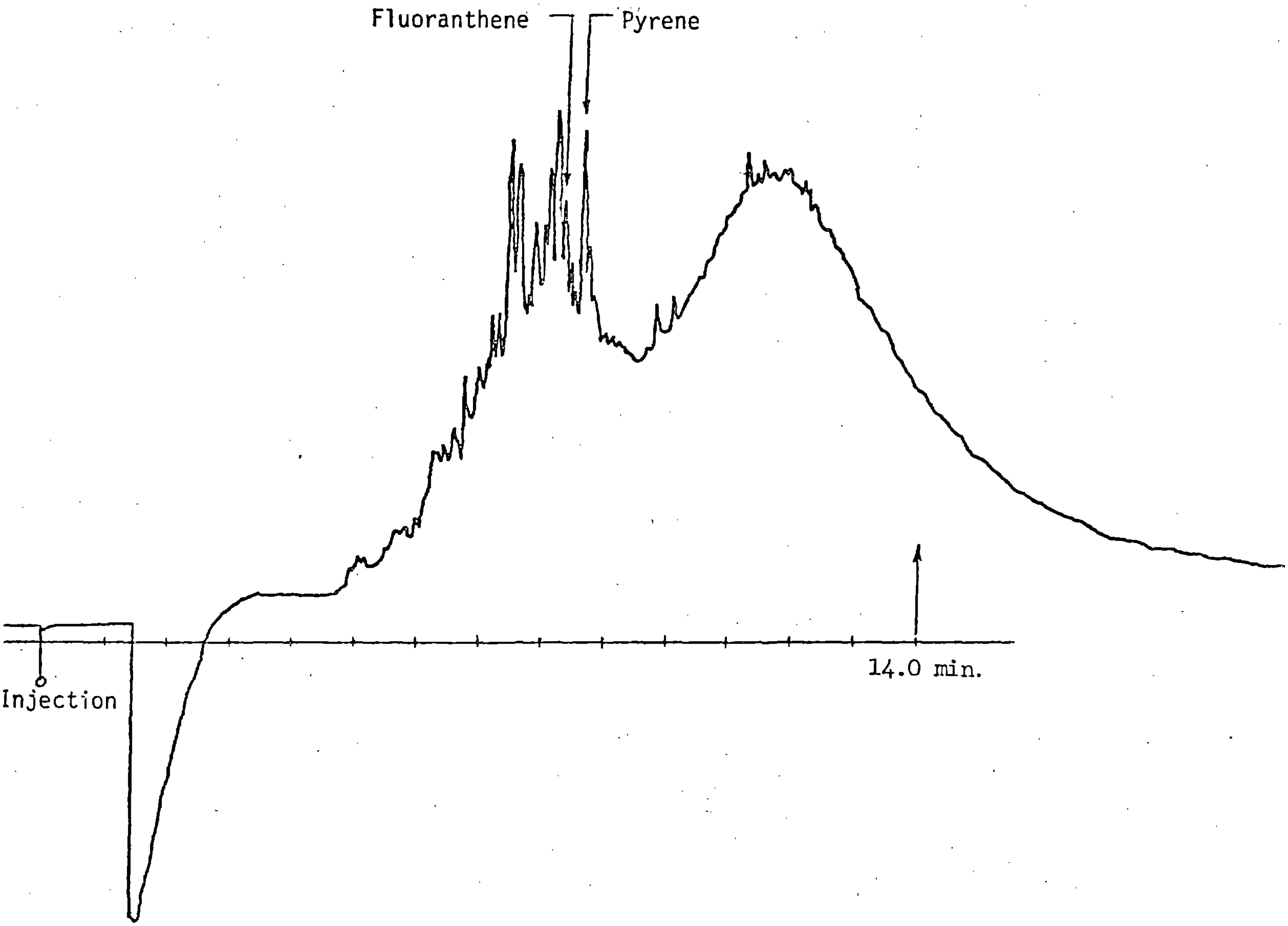

Figure II. Chromatogram of a 2-μL injection of an extract of particulate diesel emissions in methylene chloride. A GC-PID with an 8.3 electron-volt lamp and a 30-meter, DB-5 phase, fused silica capillary column were used. An initial oven temperatuire of 150 °C with a 3-minute delay was followed by a 25 °C/minute rise to 325 °C and held for 4 minutes.

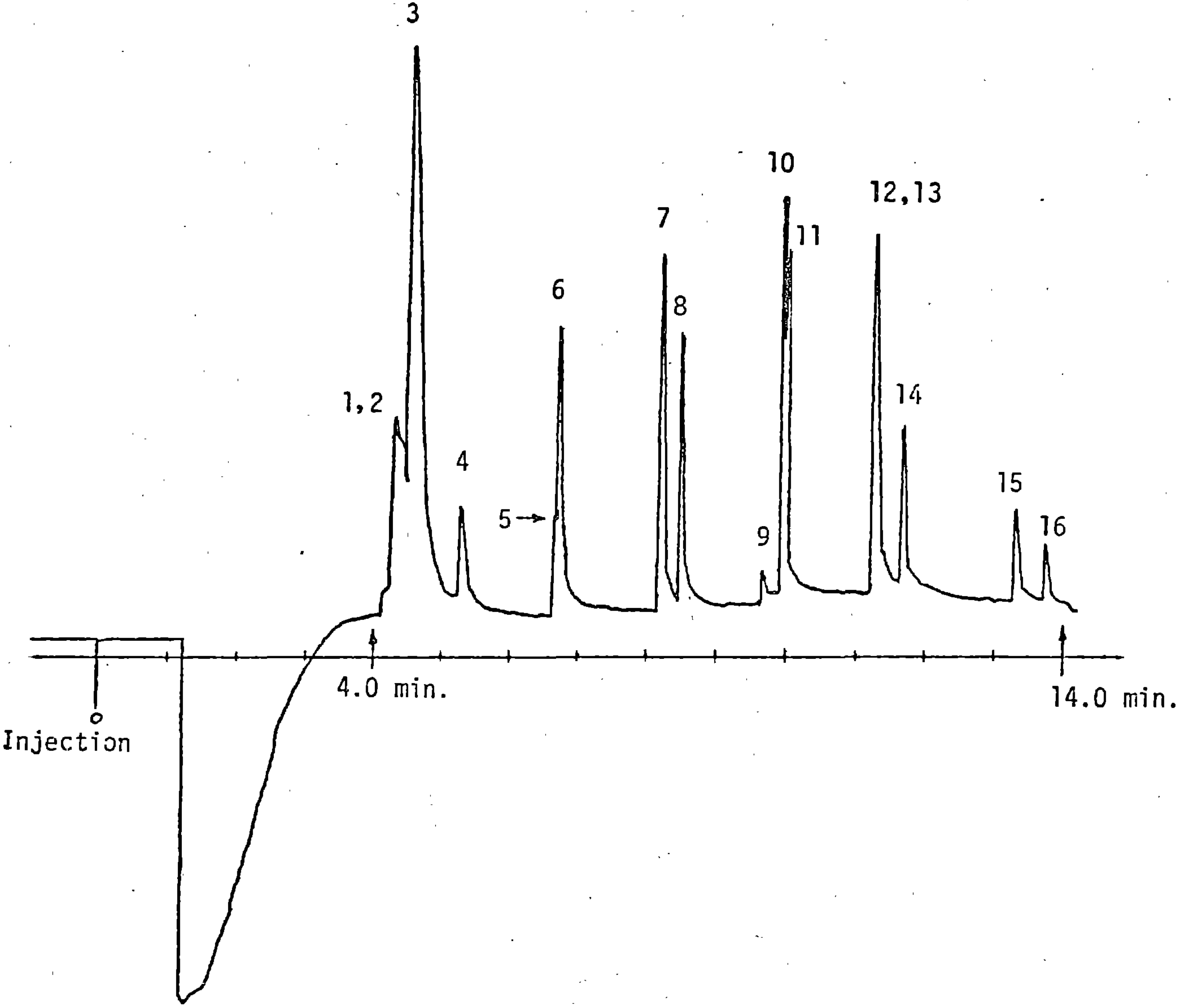

Figure III. Chromatogram of a 50-µL injection of EPA's 16-priority pollutant PAH in methylene chloride. For peak identifications and concentrations, see Table I. A GC-PID with an 8.3 electron-volt lamp and a 30-meter, DB-5 phase, fused silica capillary column were used. An initial oven temperature of 150 °C with a 3-minute delay was followed by a 25 °C/minute rise to 325 °C and held for 4 minutes.

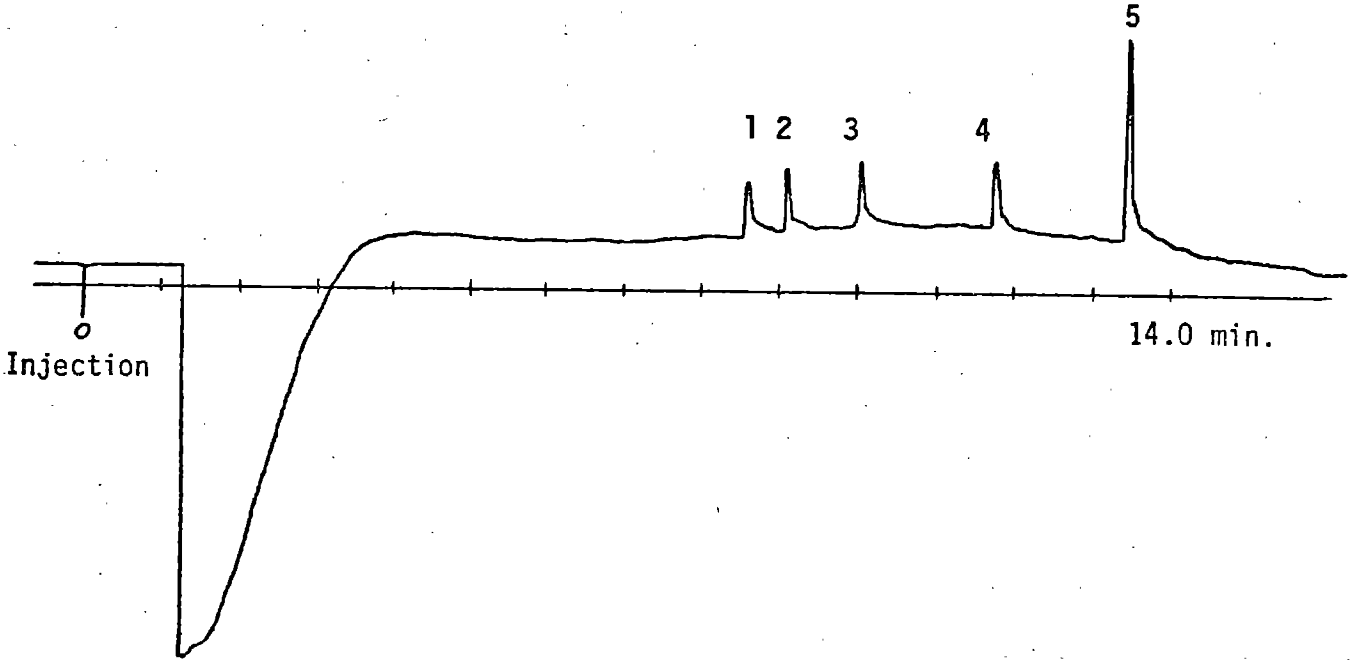

Figure IV. Chromatogram of a 50-μL injection containing: (1) 1.8-ng pyrene, (2) 2.0-ng benzo[b]fluorene, (3) 1.6-ng benz[a]anthracene, (4) 2.0-ng benzo[a]pyrene, and (5) 3.8-ng dibenz[a,h]anthracene. Retention times were 8.64, 9.14, 10.07, 11.79, and 13.47 minutes, respectively. A GC-PID with an 8.3 electron-volt lamp and a 30-meter, DB-5 phase, fused silica capillary column were used. An initial oven temperature of 150 °C with a 3-minute delay was followed by a 25 °C/minute rise to 325 °C and held for 4 minutes.

Figure V. A calibration curve for pyrene (-) was fitted to a quadratic equation. For a given peak height, the lines (---) above and below the calibration curve define a 95 $^{0}/o$ confidence range of concentrations. Injections of 50 μL were used with the instrumental conditions as found in the Experimental Section.

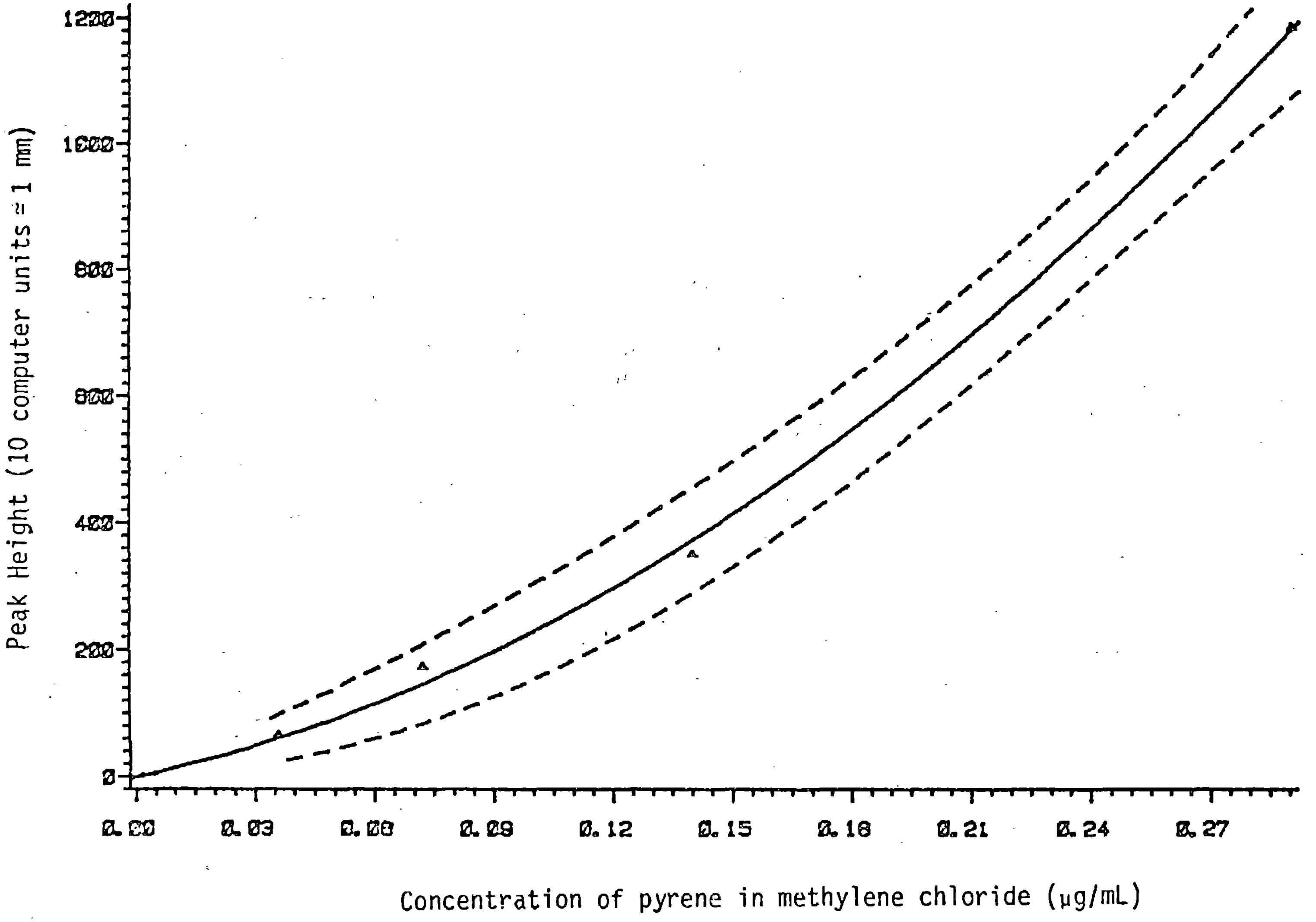

Table I. Peak identifications and concentrations for Figure III

1. Naphthalene, 0.4 μg/mL
2. Acenaphthene, 2.0 μg/mL
3. Acenaphthylene, 4.0 μg/mL
4. Fluorene, 0.4 μg/mL
5. Phenanthrene, 0.2 μg/mL
6. Anthracene, 0.2 μg/mL
7. Fluoranthene, 0.4 μg/mL
8. Pyrene, 0.2 μg/mL
9. Indeno[1,2,3-cd]pyrene, 0.2 μg/mL
10. Benz[a]anthracene, 0.2 μg/mL
11. Chrysene, 0.2 μg/mL
12. Benzo[b]fluoranthene, 0.4 μg/mL
13. Benzo[k]fluoranthene, 0.2 μg/mL
14. Benzo[a]pyrene, 0.2 μg/mL
15. Dibenz[a,h]anthracene, 0.4 μg/mL
16. Benzo[ghi]perylene, 0.4 μg/mL

Table II. Lowest detectable levels[a] for PAH in μg/mL.

Compound	LC[b]	FID[c]	Method PID(10.2eV)[d]	PID(8.3eV)[e]
Fluoranthene	0.001	-	-	0.03
Pyrene	0.005	0.1	0.1	0.02
Benzo[b]fluorene	-	0.1	0.1	0.02
Benz[a]anthracene	0.002	0.3	0.1	0.02
Chrysene	0.002	-	-	0.03
Benzo[a]pyrene	0.001	0.6	0.1	0.02
Dibenz[a,h]anthracene	-	3	0.8	0.02

(a) All lowest detectable levels represent peak heights approximately three times the baseline noise variability.

(b) LC refers to an in-house liquid chromatography technique using fluorescence detection. The data are from the notebook number 215 of our laboratory. Standards were injected onto a Vydac 201TP column and eluted using a programmed gradient with acetonitrile and water. The PAH in 25-μL injections were monitored using excitation and emission wavelengths of 297 nm and greater than 370 nm, respectively.

(c) FID refers to gas chromatography with flame ionization detection. Standards in iso-octane were injected onto a 15-meter, SE-54 coated, glass capillary column. An injection technique which included opening of the splitter vent at 0.5 minutes was used. An oven temperature program aided elution of PAH in 3-μL injections.

(d) PID (10.2 eV) refers to gas chromatography using a photoionization detector with a 10.2 electron-volt, ultraviolet lamp. Standards in iso-octane were injected onto a 15-meter, SE-54 coated, fused silica capillary column. As with the FID, an injection technique which included opening of the splitter vent at 0.5 minutes was used. The PAH in 3-μL injections were eluted using an oven temperature program. Argon was used as make-up gas.

(e) PID(8.3eV) refers to gas chromatography using a photoionization detector with an 8.3 electron-volt, ultraviolet lamp. Standards in methylene chloride were injected onto a 30-meter, non-extractable, DB-5 coated, fused silica capillary column. The PAH in 50-μL injections were eluted using an oven temperature program. Argon was used as make-up gas.

Table III. Relative standard deviations for the GC-PID and LC-fluorescence techniques for concentrations around 0.2 µg/mL.

	GC-PID[a]	LC-fluorescence[b]
Pyrene	8 ^{o}/o	36 ^{o}/o
Benz[a]anthracene	10 ^{o}/o	12 ^{o}/o
Benzo[a]pyrene	9 ^{o}/o	9 ^{o}/o

(a) Pooled RSD's for the GC-PID are given using concentrations within the range of 0.13 to 0.32 µg/mL.

(b) The ^{o}/o RSD's using LC-fluorescence were obtained from the notebook number 215 of our laboratory.

Table IV. Concentrations of PAH in ppm found by GC-PID and LC-fluorescence techniques for a sample of road asphalt.

	Method[a]	
Compound	GC-PID	LC-fluorescence
Phenanthrene	<20	2.3
Anthracene	<10	0.9
Benzo[b]fluoranthene	<20	5.2
Benzo[k]fluoranthene	<20	2.4
Fluoranthene	23.2	6.0
Pyrene	15.2	6.1
Benz[a]anthracene	<10	3.5
Chrysene	9.4	7.9
Benzo[e]pyrene	–	6.3
Benzo[a]pyrene	<20	8.0

(a) The concentrations under GC-PID pertain to the chromatogram shown in Figure I. Under LC-fluorescence, the concentrations for PAH are those reported in a memo by Ed. Slick, dated October 16, 1981, subject, "Analyses of Bulks for Polynuclear Aromatics."