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PRELIMINARY RESULTS FROM SECOND-DERIVATIVE ABSORPTION SPECTROMETRY APPLIED TO MONITORING OF PNA

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DISCLAIMER

PRELIMINARY RESULTS FROM SECOND-DERIVATIVE ABSORPTION SPECTROMETRY APPLIED TO MONITORING OF PNA*

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Second-derivative UV-absorption spectrometry shows considerable promise as a means of monitoring the more volatile polynuclear aromatic compounds (PNA's) in the vapor phase as well as the higher boiling point PNAs dissolved in a solvent such as cyclohexane. This technique provides considerable improvement in selectivity of narrow-band absorption peaks relative to direct absorption spectrometry. Figure 1 illustrates the enhancement capability of second-derivative spectrometry for narrow absorption peaks. When coupled with digital data analysis, such as linear least-squares fitting, the selectivity is sufficient to analyze accurately a rather complex mixture of PNA compounds without prior chromatographic separation.

Details of second-derivative spectrometry and of the wavelength modulated commercial instrument used in this work may be found elsewhere.[1-5] Simply stated, the technique involves sinusoidal modulation of the light source and detection of the second harmonic of the modulation frequency, which is proportional to the curvature of the sample absorption peak. The relationship between the measured signal and concentration is linear over a wide range.

When the variation of measured response with concentration is constant as a function of wavelength for all the compounds in a sample mixture, the powerful technique of linear least-squares analysis using component

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spectra can be applied to obtain an accurate analysis of a relatively complex mixture of PNAs. This requirement for concentration proportionality with wavelength is met when the absorbance of all the compounds in the sample is small ($A<<1$) or when the measured response has been properly modified as discussed in reference 5. In order to apply the least-squares method to the spectra obtained from a wavelength modulated spectrometer, the analog output signals must be digitized for input to a digital computer.

Experimental measurements were made with a Lear Siegler SM400 derivative spectrometer. The instrument is a wavelength modulated, second-derivative UV-absorption spectrometer equipped with a heated 1-m multipass (up to 32-m pathlength) sample cell for monitoring vapor phase pollutants, and a sample holder for analyzing liquid samples using a quartz cuvette (see Fig. 2). Initial measurements indicated the desirability of recording and analyzing the spectral data using digital techniques instead of the analog signals and a chart recorder. By using digital data storage, the useful dynamic range of a single scan was increased so that both intense and weak peaks could be meaningfully obtained in the same measurement. Digital data storage also allowed repeated scanning to provide spectrum averaging, which improved the signal-to-noise (S/N) ratio and, in addition, permitted digital data analysis by least-squares fitting.

Data were digitized by coupling the analog output of the spectrometer to a voltage-to-frequency converter (V/F) and counting the output of the V/F for fixed time intervals. This procedure also decreased noise by

providing some integration of the signals. The important parameters for the V/F were linearity (0.05%) and maximum frequency (100 kHz). When this method is used to digitize data, the dynamic range and recording time are interrelated and depend upon the maximum frequency of the V/F.

A multichannel analyzer (MCA), operating as a multichannel scaler, recorded the digitized signals. Dynamic and wavelength range were controlled by the dwell time chosen. Data from the MCA were recorded on a teletype that also provided a punched paper tape for data storage and for input to a time-share computer.

Calibrations of the instrument for both vapor phase and liquid solution analyses were performed. The desired vapor concentration of a compound was generated by using a pump-driven syringe filled with a known concentration of the compound dissolved in cyclohexane and injecting at a known flow rate into a heated inlet line to the multipass sample cell. The compound was vaporized and diluted to the desired concentration in air by flowing heated air over the end of the syringe. The concentration could be varied by changing the injection rate and/or the flow rate of air. For liquid analysis using the quartz cuvette, samples of desired concentration were obtained by repeated dilution of a known concentration of the compound in spectrograde cyclohexane prepared by dissolving an accurately measurable amount (about 1 mg) of the compound in the solvent. This procedure of repeated dilutions undoubtedly added some inaccuracy and imprecision to the liquid calibration samples of low concentration. A single dilution, however, to produce concentrations of a few ng/ml would consume an extravagent amount of spectrograde solvent.

Data analysis was performed using the linear least-squares procedure previously outlined.[5] A PDP-10 time-share computer was used to run the least-squares computer program.

Figure 3 shows a typical calibration curve obtained using the 1-m sample cell to measure vapor phase naphthalene. Naphthalene is an abundant constituent of coal tar and has an Occupational Health and Safety Administration (OHSA) concentration limit of 10 ppm when present in the gas phase. These measurements were made using a 12-m pathlength and a heating jacket around the sample cell to prevent condensation in the chamber. The principal absorption peak for naphthalene occurs at 222 nm and can readily be measured by means of either analog recording and graphical data analysis or digital data storage and least-squares analysis. As seen from the calibration curve, quite low concentrations of naphthalene vapors can be monitored with this instrument. Figure 4 is a spectrum taken of a 5-ppb naphthalene concentration showing a rather distinct peak at 222 nm, even at this concentration level. Similar sensitivity is obtained for liquid samples. Figure 5 illustrates the S/N ratio for a 1 ng/ml sample of anthracene in the liquid phase. Many PNAs are expected to have minimum detectable vapor phase concentrations in the range of 1 to 10 ppb and solution concentrations for a 1-cm cell of 1 to 10 ng/ml using this instrument.

As an illustration of the analytical capabilities using the second-derivative spectrometer coupled with least-squares analysis, a mixture containing four PNAs in cyclohexane was prepared. The sample nominally contained 25 ng/ml each of anthracene, phenanthrene, chrysene, and

pyrene. Pure compounds were employed to generate "standard" spectra for use in the least-squares analysis. Spectra of both the pure compounds and the mixture were measured using a 1-cm cuvette containing ∿ 2 ml of solution. 25 Figure 6 shows the spectra obtained for each of the standard solutions. Notice the considerable variation in measured response per concentration for the different compounds, with anthracene providing ∿ 20 times more intense response at the peak near 253 nm than does phenanthrene. Also note the severe overlapping of absorption peaks between the different compounds, especially for anthracene and phenanthrene near 253 nm, which would make graphical analysis unreliable.

The measured spectrum and least-squares fit of the mixture are shown in Figure 7. Table I lists the analytical results obtained from the least-squares analysis. Although the concentration determined for the relatively less intense phenanthrene is only 76% of its true value, the least-squares program tells the user that the standard deviation σ of the phenanthrene result is greater than the others; in fact, the determined value is within 3σ of the true value.

Future plans are to include a stepping motor which will provide digital control of monochrometer settings, and thus improved reproducibility, to couple the spectrometer directly to a minicomputer for data analysis and storage, and to incorporate a microprocessor into the instrument for easier, more reliable control. Prototyping of portable, special use instruments such as a phenol water monitor is also planned.

Second-derivative UV-absorption spectrometry combined with least-squares data analysis shows potential as a method for determining the vapor phase concentrations for the more volatile PNAs, as a means of analyzing the solute extract from particulates collected on filters, and as a monitor for aqueous pollution. The possible uses of this technique in real or near real-time modes of operation in several applications make it particularly appealing for occupational monitoring of work environs and for source release monitoring.

Second-derivative spectrometry improves the selectivity of the already rather sensitive technique of UV-absorption analysis. When spectral analysis is coupled with the improved selectivity provided by using second-derivative UV-absorption, a method of analysis that is both more sensitive and selective for many PNA compounds is obtained.

References

1. R. N. Hagar, Anal. Chem. 45, 1131A (1973).

2. D. T. Williams and R. N. Hagar, Appl. Opt. 9, 1597 (1970).

3. A. M. Garcia, Second-Derivative Spectroscopy as an Analytical Tool for Gas Measurements, Abstracts of the First ORNL Workshop on Polycyclic Aromatic Hydrocarbons: Characterization and Measurement with a View Toward Personnel Protection, ORNL/TM-5598, 35 (1976).

4. A. R. Hawthorne and J. H. Thorngate, submitted to Environ. Sci. Tech.

5. A. R. Hawthorne and J. H. Thorngate, submitted to Appl. Opt.

Table I. Least-squares analysis of a mixture of four PNAs

Compound	Nominal concentration (ng/ml)	Least-squares analysis (ng/ml)
Anthracene	25	25.4 ± 0.2
Chrysene	25	25.0 ± 0.7
Phenanthrene	25	18.9 ± 2.6
Pyrene	25	28.2 ± 0.6

Figures Captions

77-9343	1.	Illustration of second-derivative enhancement of narrow peaks and suppression of broad peaks.
77-9342	2.	Optical schematic diagram of the SM-400 derivative spectrometer showing both the vapor-phase-cell and liquid-phase cell modes of operation.
77-4687	3.	Analytical curve for naphthalene vapor.
77-4686	4.	Second-derivative spectrum of naphthalene vapor at a low concentration using a 12-m pathlength.
77-4685	5.	Second-derivative spectrum of anthracene in cyclohexane using a 1-cm cuvette.
77-4689	6.	Calibration standards for four PNAs in cyclohexane.
77-4688A	7.	Comparison of least-squares spectral fit to experimental spectrum.

ORNL-DWG 77-9343

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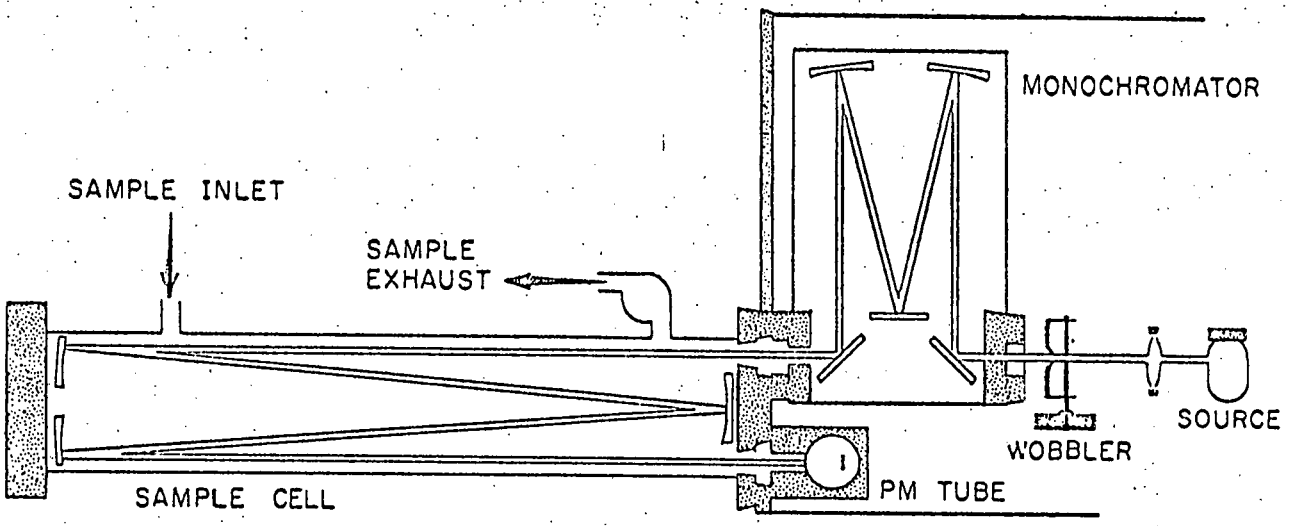

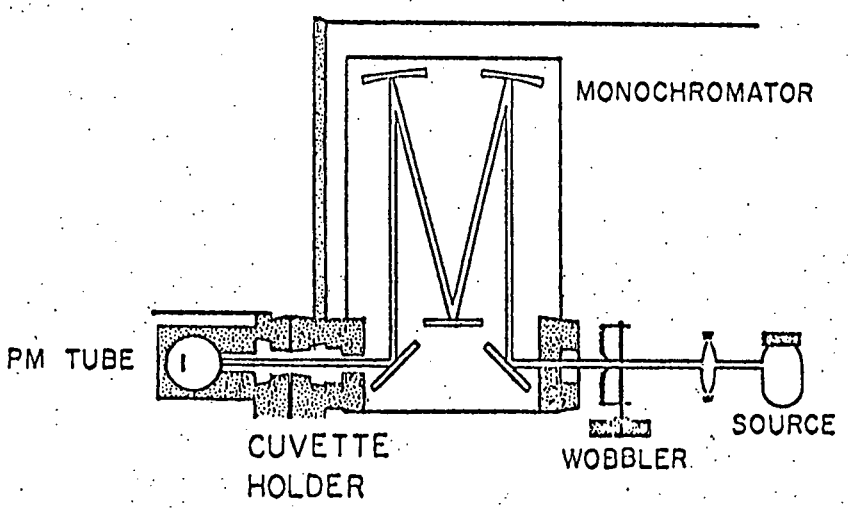

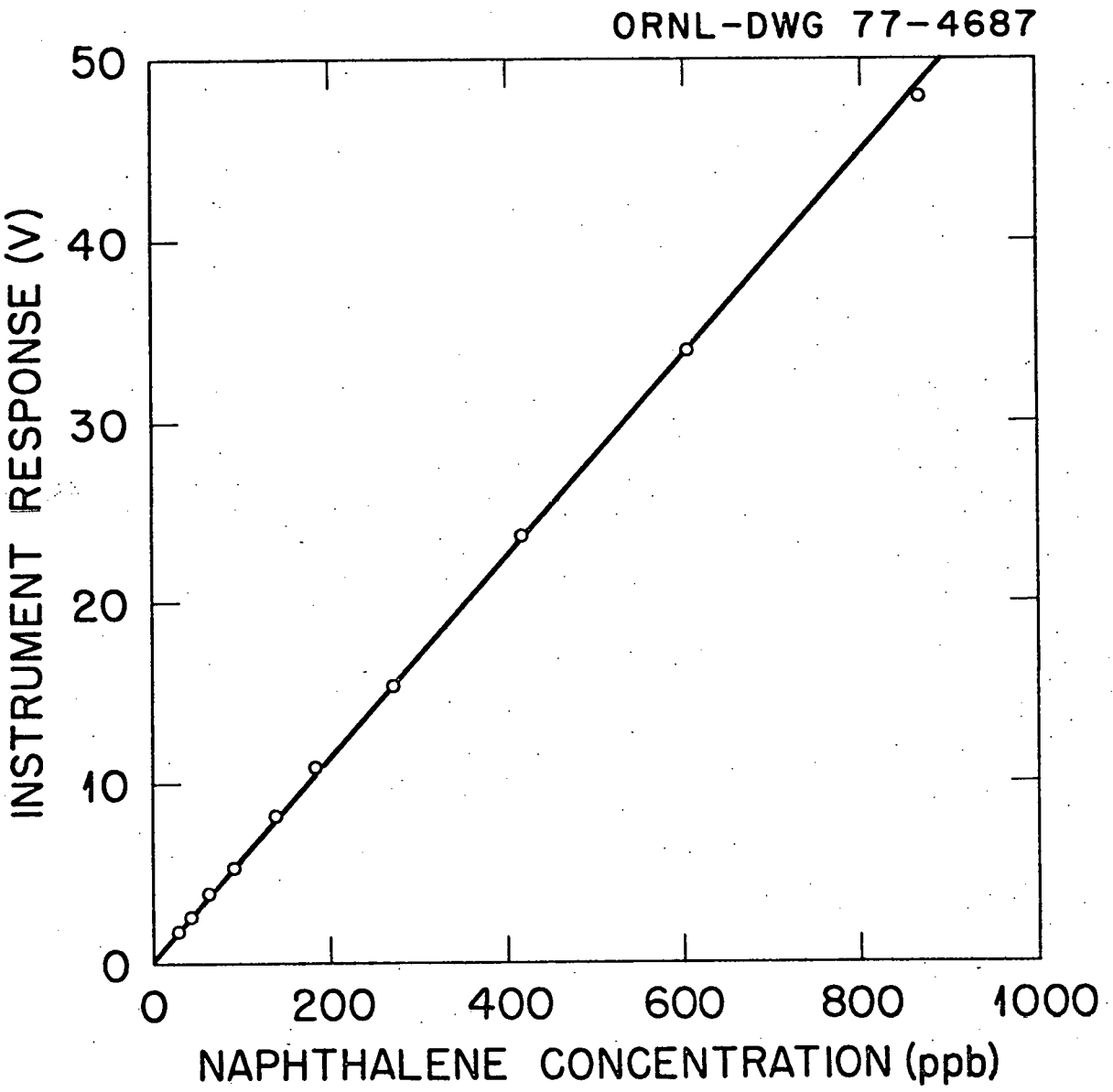
ORNL-DWG 77-4687
INSTRUMENT RESPONSE (V)
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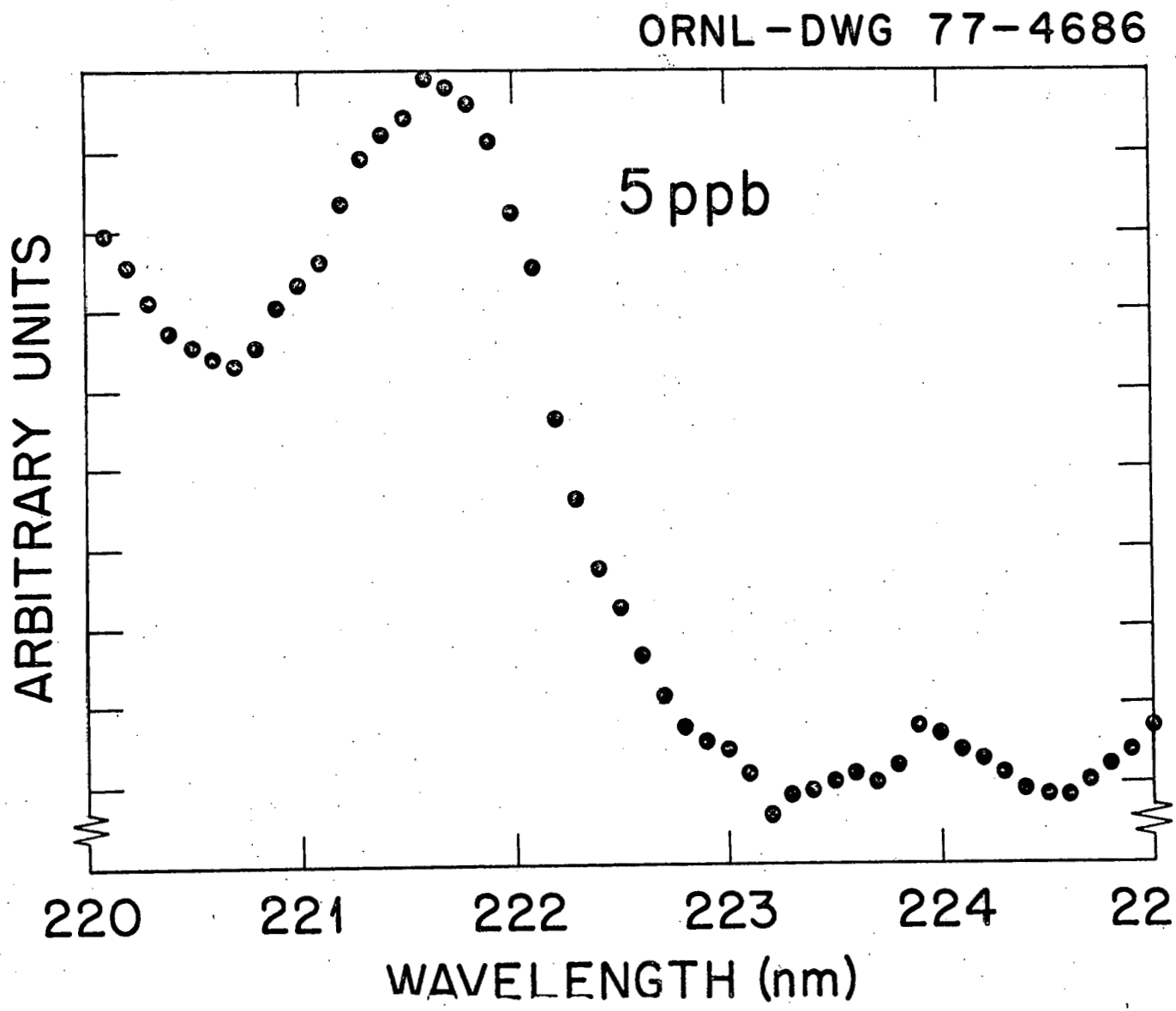
30
20
10
0
0
200
400
600
800
1000
NAPHTHALENE CONCENTRATION (ppb)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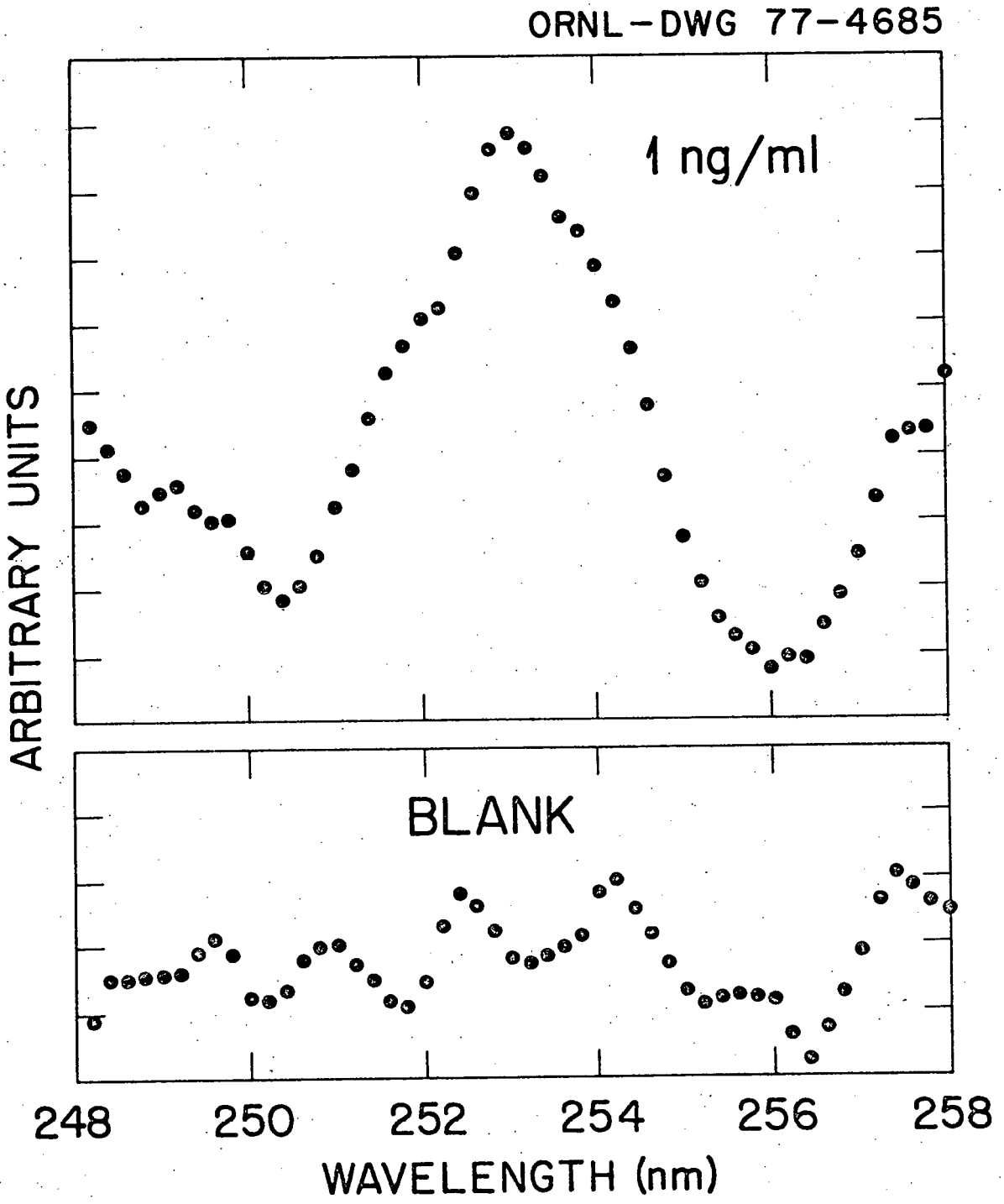
221
222
223
224
22
WAVELENGTH (nm)


ORNL-DWG 77-4685
1 ng/ml
BLANK
ARBITRARY UNITS
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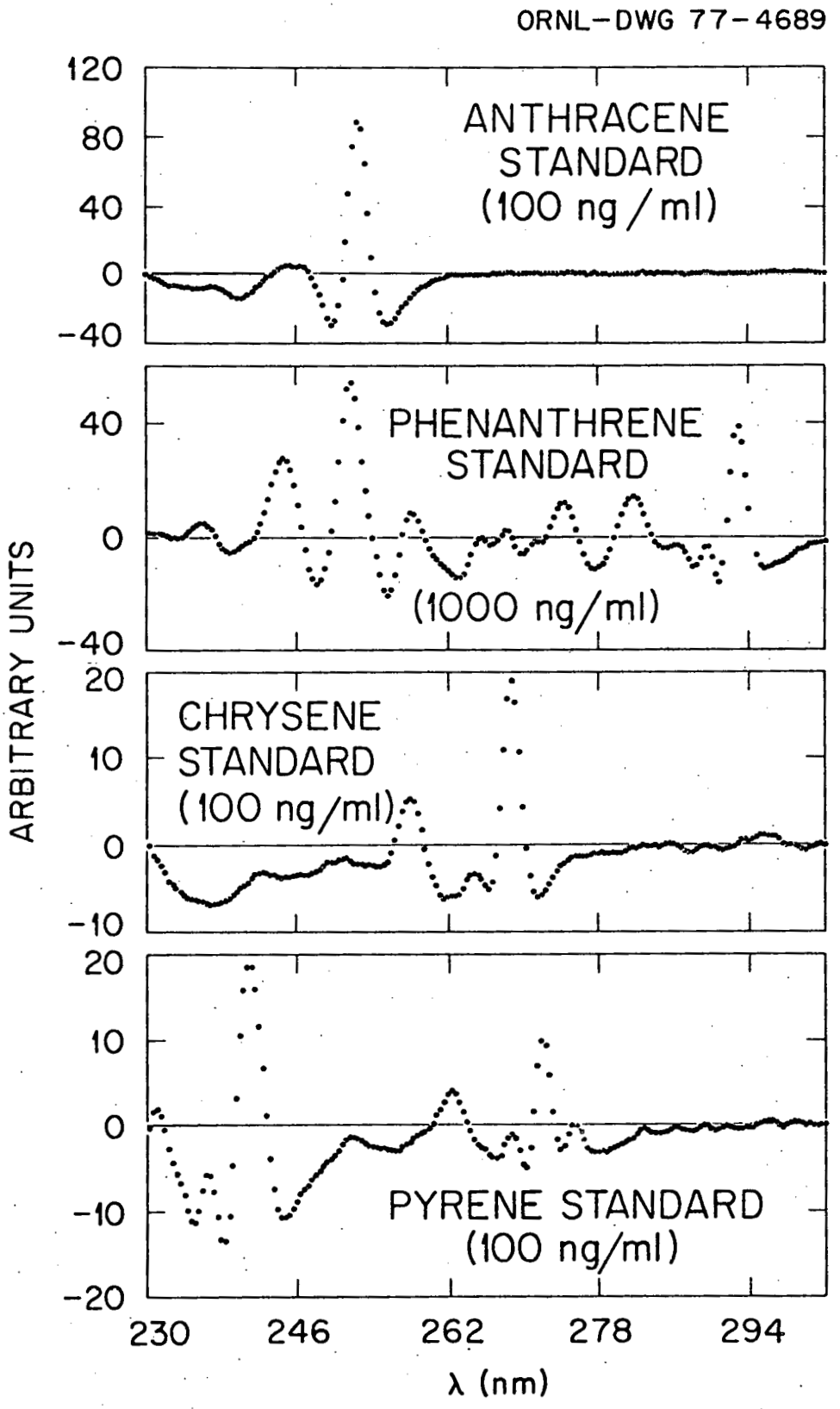
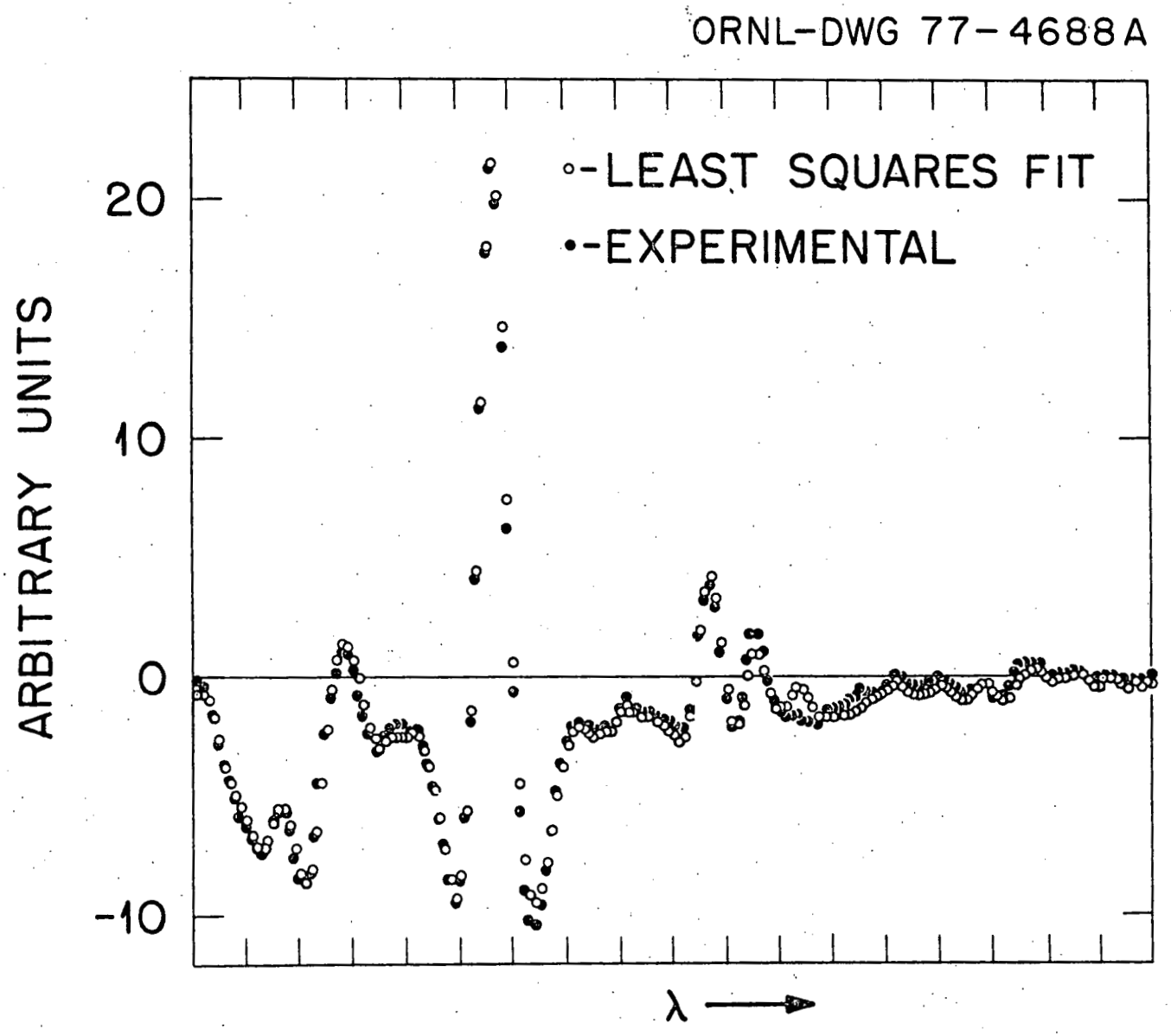
250
252
254
256
258
WAVELENGTH (nm)


ORNL-DWG 77-4689
ANTHRACENE STANDARD (100 ng / ml)
PHENANTHRENE STANDARD (1000 ng/ml)
CHRYSENE STANDARD (100 ng/ml)
PYRENE STANDARD (100 ng/ml)
ARBITRARY UNITS
λ (nm)
120
80
40
0
-40
40
0
-40
20
10
0
-10
20
10
0
-10
-20
230
246
262
278
294


ORNL-DWG 77-4688A
o-LEAST SQUARES FIT
•-EXPERIMENTAL
ARBITRARY UNITS
20
10
0
-10
λ