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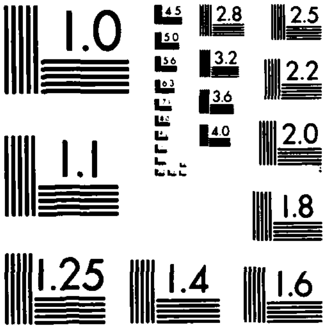
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In-Situ Fluorescence Detection of Polycyclic Aromatic Hydrocarbons Following Preconcentration on Alkylated Silica Adsorbents

Prepared for publication in <u>Analytical Chemistry</u>

by

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July 31, 1987

IN-SITU FLUORESCENCE DETECTION OF POLYCYCLIC AROMATIC HYDROCARBONS FOLLOWING PRECONCENTRATION ON ALKYLATED SILICA ADSORBENTS

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Abstract

In-situ detection of analytes sorbed to alkylated silica is found to be a sensitive and quantitative method for the determination of trace concentration levels of PAH compounds in aqueous solution. The method is developed using pyrene as a model analyte preconcentrated from methanol-water solutions onto C18 chromatographic silica, a material which is compatible with in-situ fluorescence detection of sorbed species. Adjustment of solution phase composition is shown to control the preconcentration factor by three orders of magnitude, predictable by chromatographic retention results. Sensitivity increases for fluorescence detection of pyrene within practical limits were as large as 245, leading to a 200-fold reduction in detectable solution concentrations to levels as low as 0.17 parts-per-trillion. The technique could be readily extended to the determination of a variety of PAH compounds in aqueous environments, where samples would be prepared by dilution with small quantities of methanol prior to their preconcentration and measurement. In-situ fluorescence detection has also been found to be suitable for determining the retention of solutes in regions of solvent composition where chromatographic measurements would prove difficult.

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BRIEF

Concentration detection limits were lowered relative to solution phase measurements by factors of 200, to sub-part-per-trillion levels.

Sample preconcentration as a means of decreasing concentration detection limits is a well established technique in the trace analysis of both organic and inorganic substances (1-3). Traditional methods of sample preconcentration involve liquid-liquid extraction, solvent evaporation or both, followed by separation and analysis (2). Drawbacks to this approach include loss of volatile components during evaporation (3) and incomplete extraction of trace materials from solution. More recently, trace materials have been removed from gas (4) or liquid matrices (5-8) by surface adsorption onto a variety of solid supports including cellulose (9), carbon (4,10-13), fiberglass (14), zeolites (15), membrane filters (16), Chelex 100 (17), XAD (18-20) and Tenex (21) resins and glass or silica gel derivatized with C18 (5,8,22) and other functional groups (17,23,24). Analytes have been adsorbed to a surface either directly (4,6,7,15-19) or in conjunction with chelating agents (5,8,22,25). In other applications, sorption occurs through chemically specific interactions with chelating agents immobilized on the surface of a glass support (9,17,20,23,24).

For the most part, trace materials preconcentrated through surface sorption are stripped from the support material before analysis. The extracted sample, often containing a number of components, is chromatographically resolved before detection. In-situ detection of preconcentrated analytes on the surface of an adsorbent has been demonstrated using electron spectroscopy and X-ray fluorescence (13,24). Advantages of in-situ detection of preconcentrated analyte include the reduction in losses that might occur during sample stripping and the simplification of the analytical method by eliminating a step in the procedure. In addition, removal of analyte from the adsorbent by a solvent washing step will increase the volume in which the sample is dispersed, reversing to some degree the benefits of preconcentration.

In this work, the concept of in-situ detection of preconcentrated analytes is extended to fluorescence spectroscopy; trace levels of a model PAH compound (pyrene) are preconcentrated from methanol-water solutions by sorption onto a C18 derivatized porous silica packing. The application of C18 silica columns to the preconcentration of PAH compounds from environmental samples has been demonstrated (26). This sorbent material also provides a matrix which is compatible with in-situ fluorescence detection of adsorbed species. The extent of analyte preconcentration is governed by the reversed-phase retention of pyrene on the derivatized surface which is controlled by the percentage of an organic modifier, in this case methanol, present in the solution phase. The concentration of PAH sorbed to the surface can be related to the solution concentration through knowledge of chromatographic retention values measured on a column packed with the same C18 derivatized silica.

Experimental Section.

Instrumentation. The concentration of pyrene in solution and sorbed to a reversed-phase sorbent was measured using both a Farrand Model 801 spectrofluorimeter (Farrand Optical Co., Valhalla, NY) and a laser fluorimeter described below. The spectrofluorimeter was equipped with a 150W Xenon arc lamp and monochromator set at 335 nm with 10 nm bandpass for sample excitation. Fluorescence emission was scanned with an emission monochromator having a 10 nm bandpass and detected with an RCA 1P28B photomultiplier tube. The current output of the detector was amplified and recorded on a strip chart. Fluorescence intensities were measured directly from the chart paper.

A diagram of the laser fluorimeter is shown in Figure 1. A krypton ion laser (Inova model 90-K, Coherent Inc. Palo Alto, CA) operated in the ultraviolet with emission in two lines at 351 nm and 365 nm. To eliminate the weaker 365 nm laser radiation and incoherent plasma lines, the output was dispersed with a quartz prism and undesired radiation intercepted by a barrier. An interference filter (Ealing Corp., Natick, MA) centered at 350 nm and having a bandpass of 10 nm (FWHM) was inserted into the beam path to remove any additional scattered radiation. For the majority of the experiments the vertically polarized laser beam was rotated 90 degrees with a polarization rotator (Special Optics, Little Falls, NJ) to reduce Raman and Rayleigh scatter. Intensity of the excitation beam after the polarization rotation was measured to be 60 mW.

Fluorescence emission from the sample was imaged with a 5 cm focal length glass lens through an interference filter (Ealing Corp.) having a 381 nm center wavelength and 10 nm bandpass onto the entrance slit of a 0.2 m monochromator (Instruments SA, H20V, J-Y Optical Systems, Metuchen, NJ) having a bandpass of 8 nm. A photomultiplier (Hamamatsu, model R1527, Hamamatsu City, Japan) cooled to -23 degrees centigrade and biased between 600 V and 950 V (power supply was Power Designs Inc., model 2K10) was used for the detection of radiation. The current output of the PMT was converted to voltage with a picoammeter (Keithley Instruments, model 401, Cleveland, OH) and displayed on a strip chart recorder. An RC filter with a time constant adjustable between 0.066 and 66 sec was added between the picoammeter and recorder to reduce shot noise.

Three types of sample cells were used in these experiments. The spectrometers were optimized using methanol-water solutions of pyrene in a 1 cm^2 quartz cuvette (Wilmad Glass Co., Buena, NJ). In the final evaluation of preconcentration-based analysis, the detection limits for pyrene in methanol-water solutions in quartz tubes packed with C18 silica were also compared to detection in the same tubes filled only with solvent. The tubes, custom fabricated from Suprasil-1 (Wilmad Glass, Co.) were 43 mm long, 3.2 mm outer diameter, and had an inner diameter of 0.96 mm. The quartz tubes were held in place by a brass cuvette that was similar to a previously published design (27). Improvements to the cell and the procedure for packing and preconditioning of the silica packing have been discussed in a previous publication (28). Solvent was flowed through the sample cell between 0.5 and 1.5 ml/min. The flow, controlled by an HPLC pump (Beckman, model 110A, San Ramon, CA) was kept constant at 0.5 ml/min during spectroscopic measurements and was increased to 1.0 to 1.5 ml/min when pyrene was being preconcentrated.

Chemistry. Pyrene was obtained from Aldrich and recrystallized from ethanol-water solution. Reversed-phase HPLC analysis of the compound using a 10 cm, 10 μm particle column revealed no resolvable impurities. HPLC grade methanol and acetonitrile were obtained from MCB and Burdick and Jackson. Water was purified in-house with a Corning still (MP-1) and a Barnstead cartridge purification system. The adsorbent material was ODS-2, a trifunctional, C18 stationary phase from Whatman having a carbon loading of 15.7% on a 10 μm irregular silica support (Partisil-10) with a surface area of approximately 320 m^{2}g^{-1} before derivatization. The carbon loading was confirmed in an independent analysis by M-H-W laboratory (Phoenix, AZ).

Retention measurements for pyrene under with different mobile phase compositions were carried out on a Beckman Model 110A HPLC using UV detection. A 10 cm long column was slurry packed at 7300 psi with the same manufacturing lot of ODS-2 stationary phase used in the spectroscopic measurements described above. Deuterium oxide was used as the void volume marker (29).

Results and Discussion.

Control of Surface Concentration. The uptake of analyte molecules onto a sorbent surface can be described by a distribution equilibrium constant, $K = C_s/C_m$, where C_s and C_m are the concentrations of solute in the sorbent and mobile phases respectively. Accounting for the relative volumes of two phases, V_s and V_m, one can express this equilibrium as a mole ratio or capacity factor,

$$k' = C_sV_s/C_mV_m \tag{1}$$

which is generally measured as a ratio of the corrected retention volume of the solute to the mobile phase volume, $k' = (V_r - V_m)/V_m$. If the value of k' is large, then a significant increase in concentration of analyte can be produced on a sorbent surface if the concentration in the mobile phase is maintained at C_m. A convenient means of maintaining this condition is to pass a volume of solution containing the analyte over the sorbent surface until further uptake of analyte has ceased. Analogous to frontal elution chromatography, the solution concentration at the end of the sorbent column rises to its inlet value, C_m. Under these conditions, the moles of analyte sorbed onto the surface, q_{ads}, are given by (30-32):

$$q_{ads} = C_sV_s = C_mV_{sorb} \tag{2}$$

where the sorption volume, V_{sorb}, is the break-through volume for frontal elution corrected for the void volume of the cell, V_m.

Substituting Equation 1 into Equation 2, yields a relationship between the sorption volume of a frontal analysis and the capacity factor determined by conventional chromatographic measurements with small volume injections:

$$V_{sorb} = k'\ V_m \tag{3}$$

This relationship has been verified with break-through volume measurements for alkene (32) and aromatic hydrocarbons (28) on C18 modified silica and methanol-water mobile phases for k' values as large as about 30. Deviations from the linear isotherm prediction of Equation 3 are expected to occur when the concentration of analyte on the sorbent becomes excessive; the onset of non-linear behavior has been found to occur for C18 silica when the product $k'C_m$ exceeds 10^{-2} M (32).

The greater concentration of analyte adsorbed to the surface of a sorbent may be used to increase the sensitivity of spectroscopic detection if the sorbent matrix is compatible with the spectroscopy of interest. If the sorbent surface is equilibrated with the analyte solution using a volume which exceeds V_{sorb}, then the total moles of analyte within the sample cell, q_{tot}, includes the adsorbed fraction, q_{ads}, and the solution phase contribution, C_mV_m:

$$q_{tot} = (k' + 1)\ C_mV_m \tag{4}$$

The sensitivity is governed by k', the magnitude of which depends on the relative affinity of the solute for the sorbent and solution phases. For compounds such as polycyclic aromatic hydrocarbons sorbed to reversed-phase surfaces, the value of k' depends largely on hydrophobic interactions (33,34) which can be controlled by the fraction of organic modifier in solution.

An illustration of the solution phase composition controlling sensitivity is shown in Figure 2, where the total fluorescence intensities from a series of methanol-water solutions, containing 9.7×10^{-8} M pyrene and sorbed to a C18 stationary phase, are plotted with the values of (k' + 1) determined by chromatographic elution of small volume injections. The fluorescence intensity, which is proportional to q_{tot}, follows the composition dependence of (k' + 1) as predicted by Equation 4. The results indicate that concentration sensitivity enhancements nearly as large as $k' = 10^4$ are possible for large PAH compounds on C18 adsorbents using high volume fractions of water in the solution phase.

For solutions having more than 40% water, the chromatographic determination of k' becomes tedious due to the large elution volumes required while frontal elution through the small volume spectroscopic micro-column remains tractable. At 100% water, for example, the k' for pyrene estimated from the fluorescence intensity is 6.0×10^3. A typical 10 cm chromatographic column having a mobile phase volume of 0.5 ml would require more than 3.0 l of solvent and 50 hours to elute pyrene under these conditions; the spectroscopic column, on the other hand, had a mobile phase volume of 20 µl and required a bit more than 120 ml and 2 hours time to reach a steady-state fluorescence signal. In-situ spectroscopic detection, therefore, provides a convenient method to estimate large values of the capacity factor when the solute of interest can be detected on column.

Quantitation and Detection. In designing a preconcentration procedure for enhancing spectroscopic sensitivity, there are trade-offs to be considered between the sensitivity increase and the corresponding volume of sample and amount of time required to achieve it. Exceedingly long sample integration times increase the likelihood of baseline drift which can be troublesome with single-beam spectrometry methods and can ultimately lead to larger limits of detection. As a result, we did not opt for the greatest sensitivity gain at the largest values of k' but rather chose integration times within which sample volumes and delay times would be tolerable. In addition, the linear flow velocity of the sample was greater by more than a factor ten than the value for optimal chromatographic performance; this made the sigmoidal rise in surface concentration less sharp but greatly reduced the time required to achieve a steady-state signal.

An example of in-situ detection of a preconcentrated sample of pyrene from a 55% methanol-45% water solution is shown in Figure 3. The value of the capacity factor for this solvent mixture is k' = 160 determined from the chromatographic data in Figure 2. Based on the relative lengths and diameters of C18 packing in a chromatographic column and the spectroscopic micro-column and a measurement of the void volume of the former by deuterium oxide elution, the void volume of the spectroscopic cell was estimated to be V_m = 17 µl. Using these values and Equation 3, one would expect the sorption volume to be V_{sorb} = 2.7 ml, which is close to the observed sorption and desorption volumes of 2.6 and 2.4 ml in Figure 3. This result verifies that the sorption isotherm is linear even under large k' conditions for 100 n$\underline{M}$ sample concentrations.

At a flow rate of 1 ml/min, the total time required to sorb and desorb a sample is about 10 minutes. Although the total time elapsed for this measurement is not excessive, quantitation of the adsorbed sample must be made relative to a sample-free baseline, and the five minute time between the baseline and peak signal still allows opportunity for baseline drift. While the sorption step cannot be reduced in time duration without sacrificing sensitivity, the desorption step can be shortened by stripping the analyte from the sorbent using a strongly eluting solvent, typically 100% organic modifier. This approach is analogous to anodic stripping voltammetry where the analyte, plated onto an electrode over a long period, is rapidly oxidized back into solution with an anodic potential step giving rise to a large, easily measured current pulse. In the present case, the greater rate of change of concentration with time allows the baseline to be more quickly established and reducing the influence of drift.

An example of solvent stripping of a preconcentrated analyte is shown in Figure 4 where a 1.8 μ$\underline{M}$ solution of pyrene is sorbed from a 25% aqueous solution of acetonitrile at a k' of 270 corresponding to a V_{sorb} = 4.6 ml. Following the development of a steady-state fluorescence signal after 10 ml of solution have been passed, the solvent is switched to 100% organic modifier, acetonitrile, in which the k' for pyrene is less than unity, and the baseline is restored within 30 seconds or 0.5 ml. For samples closer to the limit of detection, this procedure was modified to reduce the baseline offset arising from the differences in refractive index of the preconcentrating and stripping solvents which affect the scattered light intensity; following the stripping step, the sample is equilibrated with the preconcentrating solvent in absence of analyte, which adds another 30 seconds delay but establishes a correct baseline.

Quantitative evaluation of in-situ fluorescence determination of pyrene on a C18 sorbent surface was carried out by the above procedure using 50% aqueous methanol as the preconcentrating solvent and 100% methanol for stripping the sample from the C18 surface. The capacity factor of the preconcentrating solvent, which is equivalent to the preconcentration gain, is k' = 245, determined from the data in Figure 2. The linearity of determination was checked by measuring the fluorescence intensity of a series of four pyrene sample solutions spanning a thousand-fold range in concentration from C_m = 1.6 x 10^{-8} $\underline{M}$ to 1.6 x 10^{-11} $\underline{M}$. A plot of the log of fluorescence intensity versus log concentration showed no deviation from linearity, producing a linear correlation coefficient, r = 0.99992; more critically, the slope of the log-log plot over the three orders of magnitude in concentration was indistinguishable from unity, b = 0.993 ± 0.008.

Detection limits for the in-situ fluorescence method were evaluated by determining the concentration of solution phase pyrene which would produce a signal twice larger than the peak-to-peak baseline drift and noise or about eight times the standard deviation of the baseline. These limits were compared with detection directly in the solution phase without preconcentration using a 1 cm^2 fluorescence cuvette and the cylindrical, fused silica micro-column without reversed-phase packing, and the results are presented in Table I. The unpacked silica column was used for comparison so that the smaller excitation volume and greater stray light levels which could affect the preconcentration results might be more fairly compared. On the other hand, solution phase detection need not suffer from these sources of reduced sensitivity and larger background; therefore, more ideal detection conditions for these measurements are also presented.

The results in Table I show that the preconcentration of pyrene from solution yields a 200-fold improvement in detection limits over the solution phase detection in a square cuvette; this factor was observed for both the conventional lamp fluorimeter and the laser-based instrument. This improvement in detection limit is close to the factor, k' = 245, by which the concentration of pyrene in the detected volume was increased using the 50% methanol solvent mixture. Solution phase detection in the unpacked, cylindrical micro-column was nearly 1000-times poorer than a square cuvette, due primarily to the overwhelming intensity of specular reflection from the cell walls which greatly increases the shot and proportional noise associated with the blank measurement. When filled with silica packing, the cylindrical sample cell was essentially free of this large specular component which probably arises from reflections off of the concave surfaces at the back of the cell; diffuse scattering by the packing prevents the incident radiation from reaching the back of the cell. Despite the differences in sample cell geometry, therefore, the square quartz cuvette gave a more meaningful solution phase detection limit by which to project detection results using preconcentration on the C18 packing.

The laser fluorimeter detection limits were generally two orders of magnitude lower than the arc fluorimeter due to the greater excitation power density of the former. The lowest detection limits observed using laser-based excitation and sample preconcentration were 0.17 parts-per-trillion pyrene in solution or 9×10^{-13} M. If one is willing to tolerate extremely long integration times, the full 6×10^3 concentration gain of a 5% methanol preconcentrating solution could be realized. While equilibration times would be excessive (greater than two hours at 1 ml/min), detection limits could potentially be lowered by another factor 25 to solution concentration detection limits of 7×10^{-15} g/ml or 3.6×10^{-14} M.

In-situ detection of analytes sorbed to alkylated silica has been shown to be a sensitive and quantitative method for the determination of trace concentration levels of pyrene in aqueous samples. Adjustment of solution phase composition allows control of the preconcentration factor to suit the analysis. The technique could be readily extended to the the determination of a variety of PAH compounds in aqueous environments, where samples would be prepared by dilution with small quantities of methanol prior to their preconcentration and measurement. In-situ fluorescence detection has also been found to be suitable for determining the retention of solutes in regions of solvent composition where chromatographic measurements would otherwise prove tedious.

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Table I. Comparison of Fluorescence Detection Limits for Pyrene [a]

Sample Cell	Solution Concentration Detection Limit [b] (grams/milliliter)	
	Arc Lamp Fluorimeter	Laser Fluorimeter
1 cm^2 Square Cuvette	2.9×10^{-9}	3.8×10^{-11}
Unpacked Micro-column	5.7×10^{-6}	2.9×10^{-8}
Preconcentrated on C18 Silica	1.5×10^{-11}	1.7×10^{-13}

[a] in 50% aqueous methanol solution.

[b] defined as the solution concentration producing a signal which is twice the peak-to-peak baseline drift and noise; 95% uncertainty bounds on these limits, based on four determinations, are ± 6% relative.

FIGURE CAPTIONS

1. Laser fluorimeter for in-situ detection of sorbed molecules.

2. Comparison of pyrene preconcentration with chromatographic elution on C18. The solvent is methanol-water solution with the volume fraction water varying as shown on the X-axis. The measured fluorescence intensity following frontal elution of a 9.7×10^{-8} $\underline{M}$ pyrene solution, circles, left ordinate, is compared with chromatographic measurements of $(k' + 1)$, squares, right ordinate.

3. In-situ fluorescence detection of pyrene preconcentrated from 55% methanol-45% water onto C18 silica. Pyrene solution concentration is $C_m = 7.1 \times 10^{-8}$ $\underline{M}$ or 13.5 ppb.

4. Solvent stripping of preconcentrated samples. Pyrene at $C_m = 1.8 \times 10^{-6}$ $\underline{M}$ or 0.35 ppm is sorbed from a 25% acetonitrile solution starting about 4 ml to the left of the curve shown. At the point noted on the right, the solvent is switched to 100% acetonitrile, and the baseline is restored within 0.5 ml.

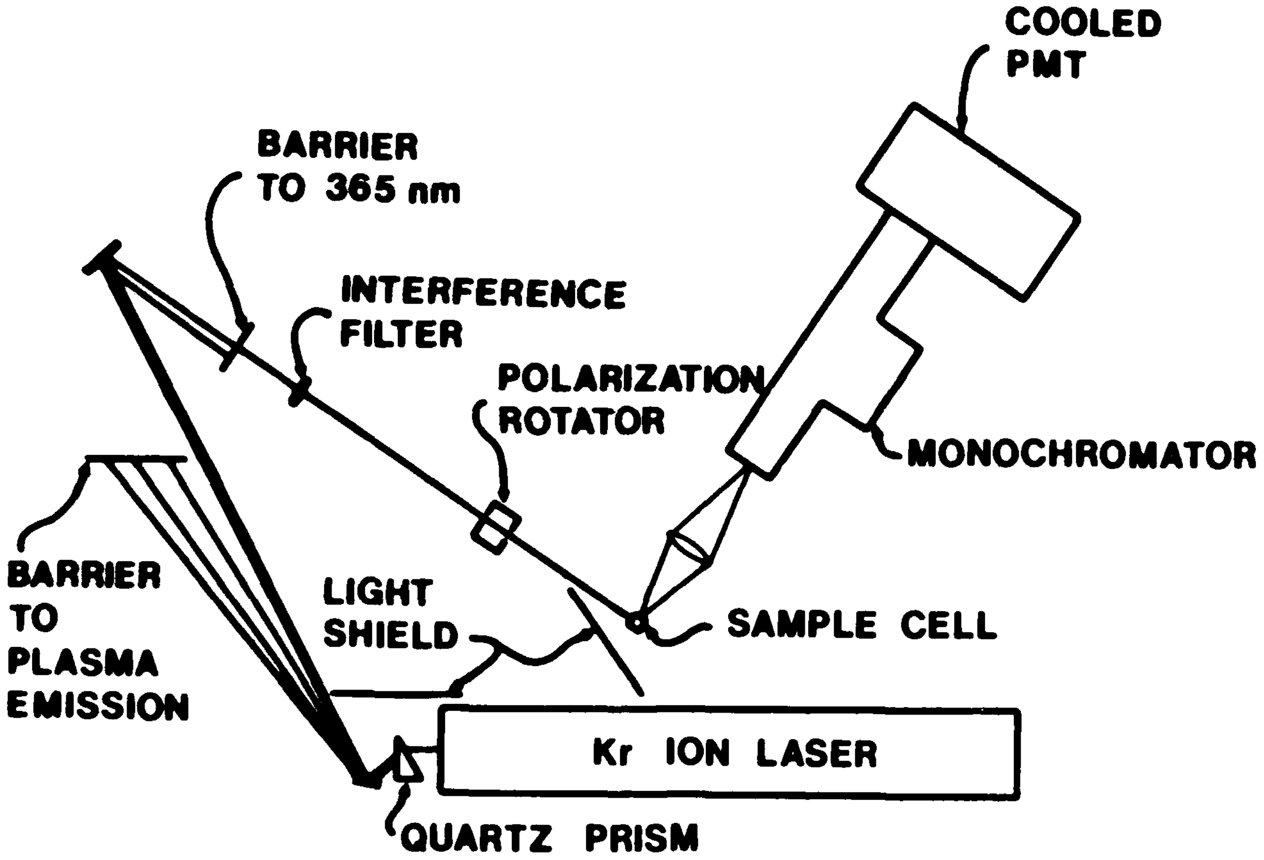
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Figure 1

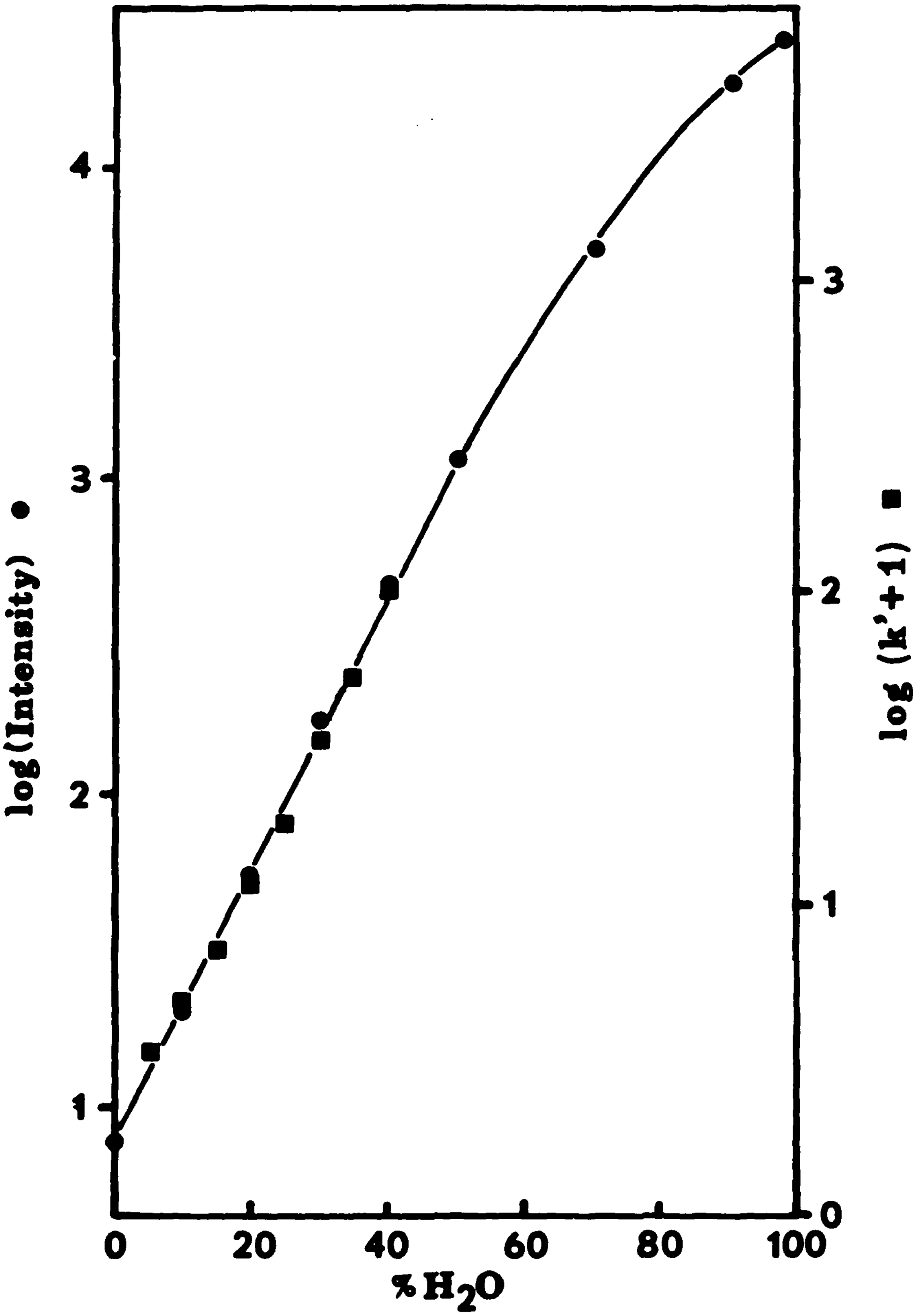
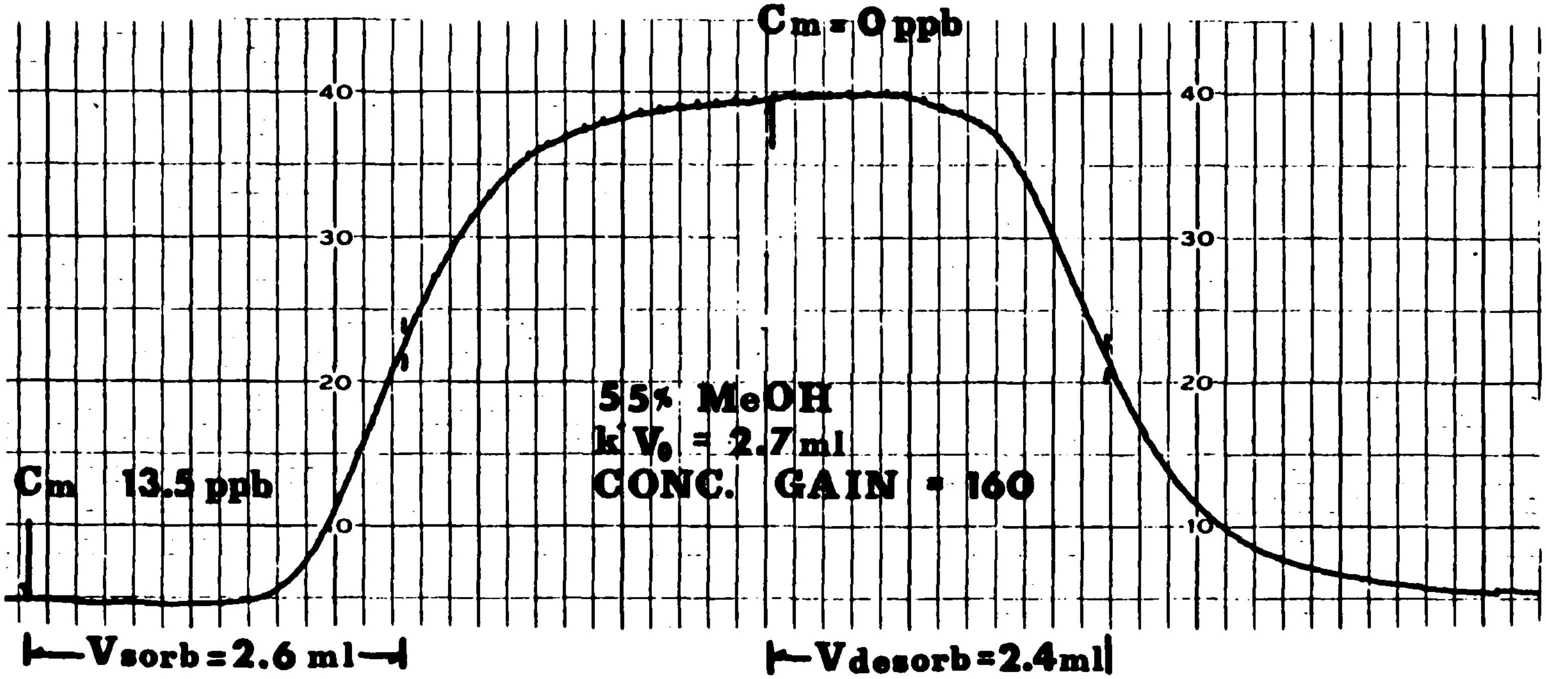


Figure 2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30
20
10
55% MeOH
k'V0 = 2.7ml
CONC. GAIN = 160
Cm 13.5 ppb
Vsorb = 2.6 ml
Vdesorb = 2.4ml

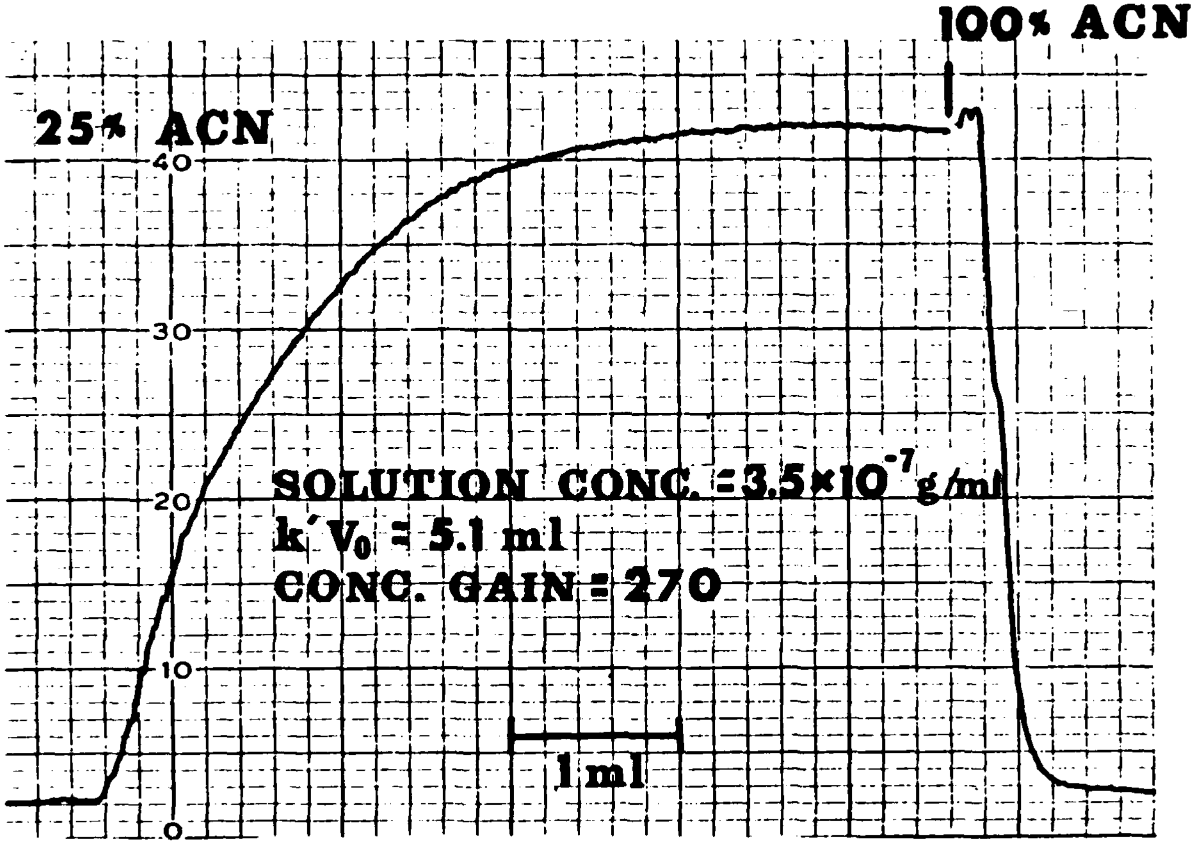
100% ACN
25% ACN
40
30
20
10
0
SOLUTION CONC. = 3.5×10^{-7} g/ml
$k' V_0$ = 5.1 ml
CONC. GAIN = 270
1 ml

Figure 4

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