of silica gel. An increase in reagent surface loading is limited by the length of plate available for chromatographic separation of reagent and product.

Figure 3 shows the plate response per hour vs. nitric oxide concentration. Each point is the average of three plate readings and standard deviations ranged from 0.18 cm at the lowest concentration to 0.45 cm at the highest concentration. A ten-plate standard deviation at 0.14 ppm NO was 0.17 cm. The graph is essentially linear between 0.05 and 0.5 ppm but exhibits a positive deviation from linearity above this range. The system therefore does not conform to simple boundary layer diffusion. However, when the plate is incorporated into a device where virtually all the diffusional resistance is in a membrane, then the plate response per hour should increase linearly with nitric oxide concentration. Sufficient sensitivity remains in the method such that a membrane may be incorporated for the measurement of typical concentrations of ambient nitric oxide.

Figure 4 shows a 24-h study for three different nitric oxide concentrations. The plate response per hour is constant for each of the two lower concentrations (0.10 and 0.28 ppm) throughout the 24-h period, whereas at the higher concentration (0.66 ppm), the plate response per hour decreases after the first 8 h. The slopes of the linear portions of all three graphs are those predicted from the calibration curve, Figure 3.

Interference Studies. Nitrogen dioxide did not react with the reagent or product radicals in the range 0.01–5.0 ppm. Sulfur dioxide did not interfere below 4.0 ppm. There was evidence that above 4.0 ppm SO_2 some deoxygenation of the reagent occurred, but the response in this concentration region was considerably below that for nitric oxide. Ozone below 1.0 ppm did not interfere. Above 1.0 ppm some unidentified brown product was produced and this did not elute with solvent. Hydrogen sulfide in a concentration range of 0–10 ppm did not interfere. Plates which were exposed to 0.48 ppm nitric oxide for 1 h at relative humidities ranging from 0–100% gave the same response. Strong light may cause photochemical deoxygenation of the reagent but this will not be a problem when a membrane is incorporated.

Temperature Studies. Simple boundary layer theory predicts that the number of moles of nitric oxide diffusing to the plate per unit time and per unit area of plate should be proportional to the square root of the absolute temperature. Plates were exposed to an atmosphere of 0.40 ppm nitric oxide in nitrogen contained in 200–300 L polyester bags. Cold rooms were used to attain the various temperatures between +23 and −23 °C. It was found that plate response appeared to vary linearly over this range, the response at −23 °C being 10.5% lower than that at +23 °C. The small change in plate response with temperature again indicates the lack of chemical control under the experimental conditions.

Present Studies. Work is continuing on mass transfer effects due to wind velocity and also on the incorporation of a suitable membrane to complete the device. These studies which are near a successful conclusion will be published shortly.

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Determination of 2,4- and 2,6-Diaminotoluene in Flexible Urethane Foams

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A fluorimetric method has been developed for the measurement of the diaminotoluenes (TDA) in flexible polyurethane foams. The precision of the method at the 20 ppm level is ±30%. TDA can be detected in foams at 1 ppm concentration. A large part of the scatter appears to be due to nonuniform distribution of TDA in foams. Using this method, we have found 2–400 ppm of TDA in 11 foams from various sources. There was 2,4-TDA in all samples, but 2,6-TDA appeared only in the conventional "hydrophobic" foams. The method consists of extraction with methanol, separation of the amines by thin-layer chromatography, and fluorimetric assay with the Fluram reagent.

Polyurethane foams derived from the toluene diisocyanates (TDIs) would be expected to contain small amounts of the corresponding diamines (TDAs). To our knowledge, no measurement of the diamines has been reported, because of their extremely low concentration.

We have developed a method which can detect as little as one part per million (ppm) of 2,4- or 2,6-TDA in flexible foams. Using this procedure, we have found 2–400 ppm of TDA in 11 commercial flexible polyurethane products. This is of interest because 2,4-TDA is included in the NIOSH list of potential carcinogens (*1*) and has been the subject of a number of toxicological studies (*2–11*). Also, the amine content of polyurethane foams is a factor in color stability, humid aging resistance, and other physical properties.

Our interest in amine analysis stemmed from measurements of aging resistance. Polyurethane foams are often used in warm, humid environments where loss of properties through hydrolysis is of concern. For this reason, some foam products have "autoclave stability" specifications such as the well-

known ASTM D-1564 steam autoclave tests for flexible polyurethanes. Direct analysis for TDA after autoclaving seemed preferable to the usual laborious measurement of compression load deflection. However, there was no published method for TDA in urethane foams, and our most sensitive method (mass spectrometry of extracts) could detect only 1000 ppm. Even severely degraded foams contained less than this amount.

Little has been published on the detection of aromatic amines in foams; almost all analytical work on TDA has been aimed at establishing the purity of the TDA used in the production of TDI. Campbell et al. (*12*) used the relative NCO and NH infrared absorptions to follow hydrolysis of TDI ureas during development of humid age compression set. Tompa (*13*) used infrared spectroscopy to study cracking of solid urethanes caused by reaction of carbon dioxide with free isocyanate. Wilson (*14*) has improved the color stability of foams by derivitizing free amines. In "Analytical Chemistry of the Polyurethanes" (*15*), the only amine method cited by David and Staley is the colorimetric method of Genchev and Atanosova (*16*). There is a potentiometric method for amines in polyurethanes (*17*, *18*), and TDA methods using gas chromatography (*19–21*), paper chromatography (*22*), thin-layer chromatography (*21*, *23*, *24*) and NMR (*25*). None of these was sensitive enough for our purpose.

Recently, Rinde and Troll (*26*) reported a colorimetric amine assay in the nanomole range, based on the Fluram reagent first introduced by Udenfriend (*27*). Amines in water or body fluids were separated by thin-layer chromatography and assayed on the plate as stable, yellow derivatives. They did not examine the diaminotoluenes, but Kottemann (*24*) used a TLC method to identify TDAs and other aromatic amines at high concentrations in hair dyes. Our method combines TLC and fluorimetry for such low concentrations of TDA that the spots are invisible in ordinary light.

EXPERIMENTAL

Reagents. Methanol and acetone were Baker reagent grade solvents. The 2,4- and 2,6-diaminotoluenes were from Eastman and Aldrich, respectively, and were used without further purification. The Fluram reagent was obtained from the American Instrument Company, 8030 Georgia Avenue, Silver Spring, Md. 20910.

Apparatus. Instruments used in this work were an Aminco-Bowman Spectrophoto Fluorimeter with a model J4-8427 thin film chromatographic scanner and a model J10-280 photomultiplier microphotometer. Attached to this was a strip chart recorder with a 10-mV full scale output.

Extraction. Polyurethane foams contain 0.1–3% of water-soluble materials which we have found to consist mainly of surfactants and linear urethane polymers. Dried aqueous extracts typically contain about 1000 ppm of TDA isomers, but aqueous extraction and evaporation is laborious. Experimentation with various solvent extraction methods showed that three 5-min extractions with methanol at room temperature were sufficient to remove the TDA from flexible foams. Freshly made foams (wet) may be analyzed immediately by this method, using the weight of the dried extracted foam as the initial foam weight.

Selection of sample size depends on the amount of TDA in the foam. For typical foams with 1–250 ppm of TDA, 1–2 g of foam is sufficient. Any convenient extraction apparatus may be used although prolonged contact with hot methanol may generate more TDA. For rapid extraction of a large number of samples, the following method has been found to be effective.

The foam, weighed to the nearest mg, is covered with 75 mL of methanol in a 250-mL beaker and soaked for 5 min with occasional compression. The methanol is decanted, squeezing the foam as completely as possible to express the methanol. This is repeated twice with fresh methanol, and the combined extracts are concentrated to 25 mL for the analysis (further dilution or concentration may be required if TDA concentration is too high or too low).

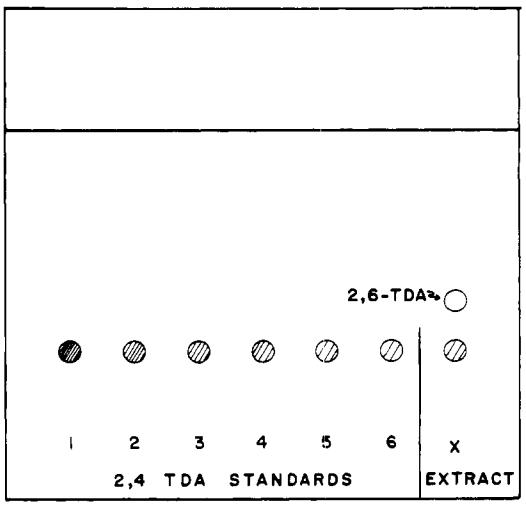

Figure 1. Positions for spotting TLC plate, and approximate positions of developed spots

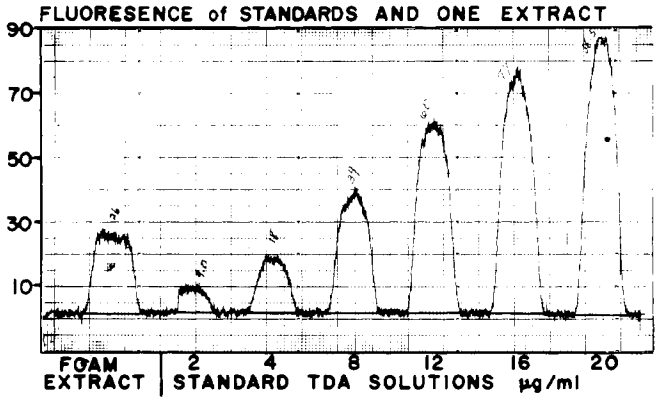

Figure 2. Typical chart readout, showing relative fluorescence of 2,4-TDA standards and foam extract

Chromatography. Solutions of 2,4- and 2,6-TDA are prepared in methanol as standards which contain 20, 16, 12, 8, 4, and 2 µg/mL. We found that acetone solutions deteriorate within a few hours, presumably through formation of ketimines. Methanol solutions are stable for weeks.

The TLC plate is marked as shown in Figure 1. The standard solutions (20 µL) are spotted at six positions 3 cm from the bottom of the plate as shown. The foam extract is spotted at the seventh position.

After the spots have dried, the plate is placed in a developing tank which contains 120 mL of chloroform, 33 mL of ethyl acetate, 20 mL of ethanol, and 7 mL of glacial acetic acid. Development takes 1 h and is complete when the developing solution reaches a line 15 cm above the bottom of the plate.

The plate is dried in a horizontal position for 5–10 min, then sprayed uniformly with a 0.015% solution of Fluram in acetone. The spots, which appear approximately 6 cm (2,4-isomer) and 8 cm (2,6-isomer) above the bottom of the plate, can be located with an ultraviolet light. We used a long-wave hand-held BLAK RAY model UVL-60 from Ultraviolet Products, Inc. The sides of the plate are marked to indicate the line through which the plate is to be scanned.

Fluorimetry. The plate is placed in the Aminco scanner and the excitation wavelength is set at 500 nm to produce a visible light spot. The plate position is adjusted so that the visible spot is in position to scan across the line of TDA spots. The cover of the scanner is closed and the excitation and emission wavelengths are set at 390 and 500 nm, respectively. The plate is then scanned, starting with the strongest standard spot to generate a chart such as that shown in Figure 2. It must be read within 1 h after development because the Fluram adducts are unstable. Although the calibration standards and the extract presumably deteriorate at the same rate, it is best to scan the plate as soon as it is developed.

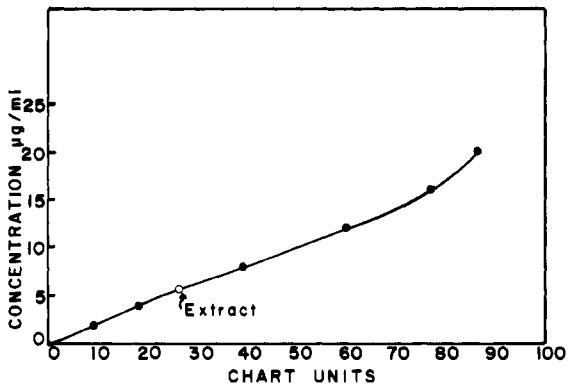

Figure 3. Illustrative plot of chart units vs. TDA concentrations using data from Figure 2

Calculation. Peak heights are measured from the baseline and are plotted as illustrated in Figure 3. The concentration of TDA in the extract is then calculated from the known concentrations of the standard solutions. To express this value as parts per million in the original foam, the following is used:

$$\text{TDA, ppm in foam} = \frac{(\text{TDA in extract, } \mu\text{g/mL})\ (\text{mL extract})}{\text{foam weight, g}}$$

In the illustration, 25.0 mL of concentrated extract from a 2.0-g foam sample contained 2,4-TDA at a concentration of 5.7 µg/mL. Using the above equation, this gave a 71 ppm TDA concentration in the foam.

The precision of this method for a given foam is at least ±30% relative standard deviation at the 20 ppm level.

RESULTS AND DISCUSSION

The identity of the diaminotoluene spots was established by comparison with R_f values of the standards run on the same plate. Also, TDA standards and spots from extracts after development, were scraped from TLC plates and placed in the solids probe of an AEI MS-12 mass spectrometer. Identical mass spectra were obtained for the standard TDA spots and those from the sample (Figure 4). The position and shape of the spot from 2,4-TDA was the same as that reported by Kottemann.

When wet, freshly made foams were extracted with methanol within a few hours of preparation, a very bright oval spot appeared on the TLC plate approximately 10.5 cm above the bottom. This was shown to be methyl (2-amino-*p*-tolyl) urethane (I, Figure 5) formed by hydrolysis of the 2-isocyanate of 2,4-TDI and subsequent reaction of the 4-isocyanate with the extractant methanol. An authentic sample was prepared by the reaction of stoichiometric amounts of methanol and 2,4-TDI at 10 °C followed by hydrolysis in dilute sulfuric acid. After neutralization and recovery of the product, it was recrystallized several times from water to give a white solid, which melted at 137–139 °C and had a correct NMR spectrum, infrared spectrum, and elemental analysis. Two fainter spots sometimes seen under the same conditions may have been the other isomer and the corresponding compound from 2,6-TDI.

Table I summarizes the TDA content of commercial or sample foams from eleven suppliers. All contained 2,4-TDA (II), but only three contained the 2,6-isomer (III) in detectable amounts. We assumed at first that this was because of the 4/1 ratio of 2,4-TDI to 2,6-TDI in commercial grades of TDI. However, work in progress indicates that the reason is more complex. The main factor may be the higher water solubility of 4-amino-2-isocyanatotoluene which allows it to become isolated in the aqueous phase of the foam where it can become hydrolyzed to the diamine. The less water-soluble 2-amino-6-isocyanatotoluene may remain in the organic phase where it is consumed in urea formation or other reactions which prevent hydrolysis to the diamine. Also, mixing conditions and maximum foam temperature have a bearing on the amount of 2,6-TDA which is formed.

Table I. TDA Content of Eleven Flexible Polyurethane Foams

Foam No.	Description	TDA ppm 2,4-Isomer	TDA ppm 2,6-Isomer
1	Hydrophilic Polyether, Type I	20	0
2	Hydrophilic Polyether, Type 2	77	0
3	Hydrophilic Polyether, Type 3	6	0
4	Hydrophobic Polyether, Type 1	67	80
5	Hydrophobic Polyether, Type 2	338	0
6	Hydrophobic Polyether, Type 3	99	0
7	Hydrophobic Polyether, Type 4	123	62
8	Hydrophilic Polyester, Very Old	20	0
9	Hydrophilic Polyester, Fresh[a]	112	0
9	Hydrophilic Polyester, Fresh	442	0
10	Hydrophobic Polyester, Type 1	27	0
11	Hydrophobic Polyester, Type 2[a]	19	8
11	Hydrophobic Polyester, Type 2	52	0

[a] Extracted with water. Note: We define a hydrophilic foam as one which will absorb a drop of water placed on its surface within a minute. These usually contain substantial amounts of poly(oxyethylene) units.

Table II. Comparison of Extraction Methods Using Hydrophilic Polyether Foam

Experiment No.	Extraction method	2,4-TDA, ppm		
1	Water, 60° C, 7 times	5.3		
2	Methanol, Soxhlet, 1 h	25	20 ± 6	20 ± 5
3	Methanol, Soxhlet, 1 h	16		
4	Methanol, Soxhlet, 1 h	16		
5	Methanol, Soxhlet, 1 h	15		
6	Methanol, Soxhlet, 1 h	29		
7	Cold methanol, 7 times	24	20 ± 3	
8	Cold methanol, 7 times	17		
9	Cold methanol, 3 times	21		
10	Cold methanol, syringe, 3 times	18		
11	Cold THF, 7 times	9		
12	Cold, THF, syringe, 7 times	12		

In general, TDA extraction is more complete with methanol than with water. Also, the TDA content may vary considerably from place to place in the same foam, and in the same type of foam which has been aged under different conditions. Preliminary work indicates the presence of more TDA near the outside of a large foam than inside, although samples taken close together are fairly uniform. For these reasons, it would be premature to state that one type of foam inherently contains more TDA or a different isomer distribution than another.

We have tested a number of extraction techniques because this is the slowest step of the method. Prolonged contact with water of alcohols could generate TDA through solvolysis, although the data in Table II indicate that this is not a problem under the conditions we have tried. When the foam

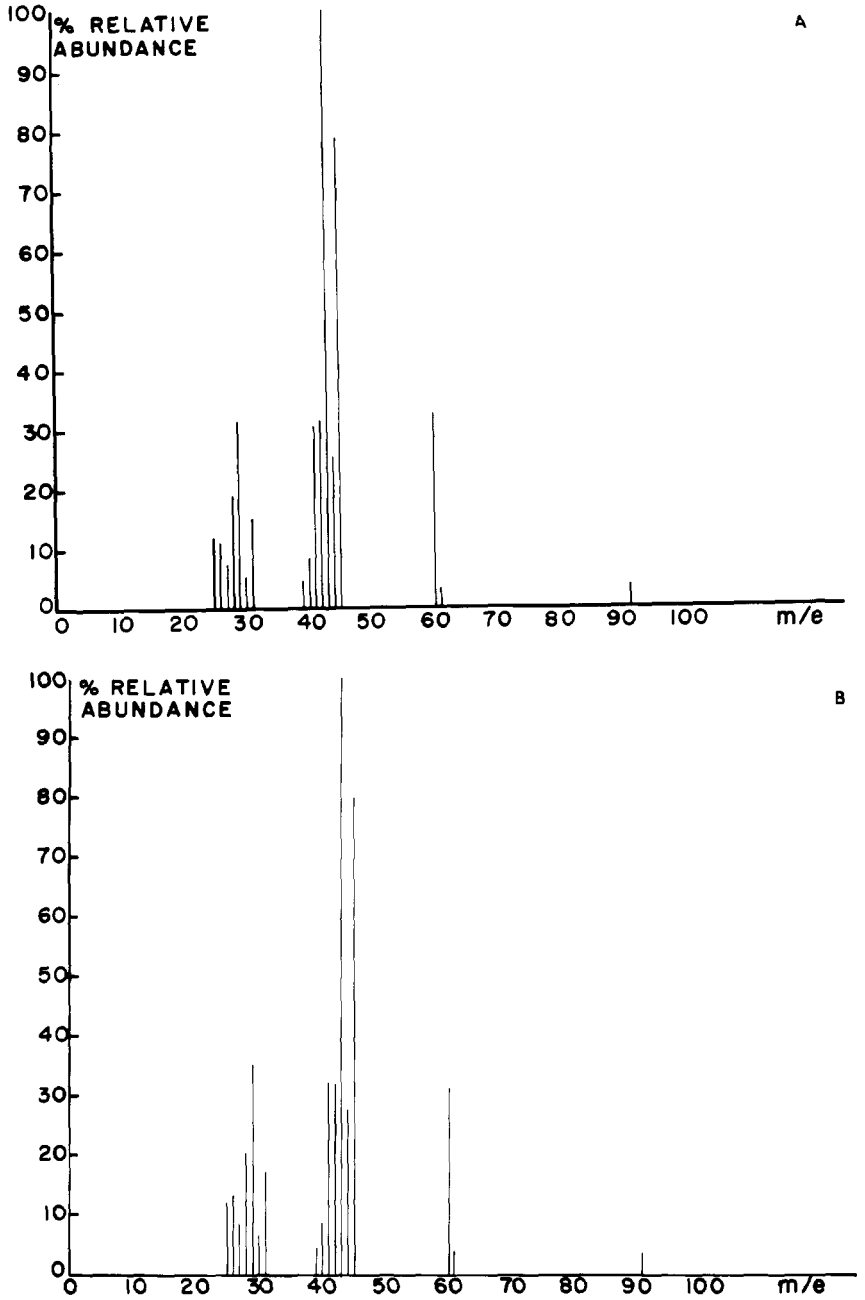

Figure 4. Mass spectra of Fluram adducts of 2,4-TDA ((A) authentic and (B) extract

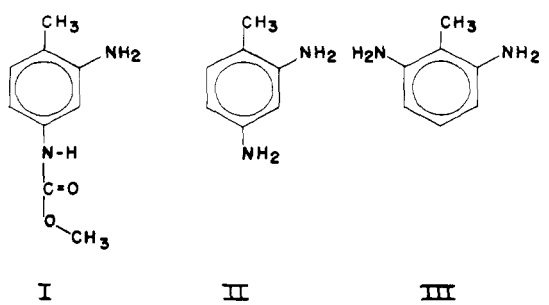

Figure 5. Structures of compounds referred to in text

used to get the data in Table II was autoclaved at 105 °C, its TDA content did not increase significantly for approximately 2 h. One rapid extraction technique is to put quarter-inch cubes of foam into a barrel of a 30-mL syringe and to suck cold methanol in and out a number of times as the foam is compressed and released. Three changes of methanol in this technique extracted as much TDA as a 1-h modified Soxhlet extraction. Tetrahydrofuran is a less effective extractant than methanol. Table II summarizes results with a single foam using various extraction techniques.

This foam was cut from the inside of an oven-dried foam. A piece from the outside of the same foam was analyzed, using the Soxhlet extraction method. Five replicates gave a TDA content of 51 ± 14 ppm; more than twice as much as was found in the inside. This phenomenon has been seen several times. It may result from the higher temperature on the inside which favors reaction of the 4-amino group with isocyanate to form ureas.

Table III shows typical results of duplicate measurements at the 10–15 ppm level. The precision, with a given extract, is usually ±10%. If different samples of the same foam are tested, the precision is usually only 30% because of non-uniformity of the foam.

We have used the same method to assay amines in urethane products derived from isocyanates other than TDI. It is

Table III. Duplicate Analyses of Extracts of Hydrophilic Polyether Urethane Foams

Foam No.	TDA in Foam, ppm	
	Plate 1	Plate 2
A	11.3	9.4
B	15.8	15.8
C	15.4	15.4
D	11.2	12.2
E	15.5	16.6
F	10.4	11.3

applicable to bis(4-aminophenyl)methane (MDA) and the aliphatic amines bis(4-aminocyclohexyl)methane (reduced MDA) and isophorone diamine. In the case of the reduced MDA, the intensity of the fluorescence is too low to detect less than 100 ppm by the present method. Obviously, the use of larger foam samples can overcome this problem. We have not yet looked for any other amines. Occasionally there is interference from polymeric amines, diethylenetriamine, 4,4'-diaminodiphenylurea, and other amino contaminants. An experienced operator can soon learn to recognize these by the shape, intensity, and position of the spots on the plate. Polymeric amines tend to stay at their initial position on the plate. Poor separations can usually be overcome by adjustments in the composition of the developing solution.

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Ultra-Trace Method for Lanthanide Ion Determination by Selective Laser Excitation

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Conventional coprecipitation techniques have been combined with laser spectroscopy to provide a new technique for trace analysis that exhibits excellent selectivity and detectivity. The technique is here applied to lanthanide ion determinations by coprecipitating the lanthanide in calcium fluoride. A series of different crystallographic sites result for the lanthanide ions because of the charge compensation required for the Ln^{3+} substituting for Ca^{2+}. Proper ignition conditions can produce an analytically useful site distribution where a single oxygen compensated site predominates. When 0.06 mol CaF_2 was precipitated from 40-mL solutions containing 50 pg/mL to 1.25 μg/mL of erbium, the fluorescence intensity from the single site was directly proportional to erbium concentration with an RSD of 8%. The estimated detection limit is 25 fg/mL of erbium. The technique is shown to be highly selective and free from interference from other lanthanide ions.

A new technique has been developed for trace analysis by selective excitation of probe ion luminescence (SEPIL). The technique requires the formation of a crystalline host lattice in the presence of a spectroscopically active ion whose transitions are sharp and dependent upon the local crystalline environment. The sharp lines permit a tunable laser to excite a specific ion in a specific site with a high selectivity. The technique can be used to determine the spectroscopically active ion directly as will be described in this paper or it can be used to determine other ions that enter the lattice and perturb the crystal field levels of the spectroscopically active probe ion as will be described in subsequent papers.

In this paper, we demonstrate the use of the technique for lanthanide ion analysis by coprecipitation in a calcium fluoride host precipitate. Although most of the lanthanide ions can be determined by SEPIL, the CaF_2:Er^{3+} system was chosen as a representative example because of the detailed studies that have been performed on single crystal samples in this laboratory and elsewhere. This information has provided the basis for a fundamental understanding of the coprecipitation–laser spectroscopy system which promoted the rational development of the analytical technique.

When calcium fluoride is precipitated in a solution containing lanthanide ions, the lanthanide ions coprecipitate and enter the lattice substitutionally at calcium sites. After the