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A flow-injection analysis (FIA) system incorporating a microcolumn of activated alumina was used for the determination of molybdenum by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The transient signal resulting from the injection of molybdenum was determined by a spectrally segmented photodiode-array spectrometer. Linear calibration was established for molybdenum over a concentration range 0 - 1000 ng/ml^{-1}. The detection capability was approximately 50 times better than offered by comparable continuous-nebulization systems. The detection limit for molybdenum was 0.2 ng/ml^{-1}, and the relative standard deviations at 500 and 10 ng/ml^{-1} were about 2 and 5%, respectively. The ability of the multichannel photodiode-array spectrometer to correct for background shifts which occur during signal integration period provided improved precision and accuracy. Application to the analysis of molybdenum in standard sea water (NASS-2) was demonstrated.

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Flow-injection analysis utilizing a spectrally segmented photodiode-array inductively coupled plasma emission spectrometer

I. Microcolumn preconcentration for the determination of molybdenum

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Abstract.

A flow-injection analysis (FIA) system incorporating a microcolumn of activated alumina was used for the determination of molybdenum by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The transient signal resulting from the injection of molybdenum was determined by a spectrally segmented photodiode-array spectrometer. Linear calibration was established for molybdenum over a concentration range 0 - 1000 ng ml^{-1}. The detection capability was approximately 50 times better than that offerred by comparable continuous-nebulization systems. The detection limit for molybdenum was 0.2 ng ml^{-1}, and the relative standard deviations at 500 and 10 ng ml^{-1} were about 2 and 5 %, respectively. The ability of the multichannel photodiode-array spectrometer to correct for background shifts which occur during signal integration period provided improved precision and accuracy. Application to the analysis of molybdenum in standard sea water (NASS-2) was demonstrated.

1. INTRODUCTION

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) has been used successfully for a wide range of applications. Although ICP-AES is a very sensitive method, its sensitivity is sometimes inadequate for the determination of trace elements in pure materials or natural waters. Moreover, when the method is applied to samples, such as sea water with high levels of dissolved salts, spectral interferences caused by the presence of alkaline earth elements are a common problem. Additionally, physical interferences resulting from the nebulization process also cause difficulties. In such cases, separation techniques and/or preconcentration procedures prior to spectrochemical analysis enhance analytical performance.

Flow-injection analysis (FIA) utilizing an on-line preconcentration column provides a novel approach for the separation and preconcentration of desired elements in the presence of an interfering matrix [1-5]. FIA is based on the injection of a discrete sample plug into a non-segmented carrier stream. Therefore, the signal obtained in FIA is transient in nature. The multichannel photodiode array detector is capable of detecting such a transient signal because of its ability to monitor simultaneously a wide spectral range.

In this paper, an acidic alumina column was used as a vehicle for preconcentration for molybdenum. The resulting deposit was eluted by an ammonia solution to produce a transient signal that was measured by a spectrally segmented photodiode-array spectrometer.

2. EXPERIMENTAL

2.1. Experimental apparatus

A schematic diagram of the FIA system is shown in Fig. 1. An alumina column was made by packing activated alumina (150-200 mesh) into a Teflon tube (i.d.: 1.5 mm, length: 50 mm). To minimize sample dispersion, the length of the tubing (i.d.: 0.5 mm, o.d.: 1.5 mm) connected to the microcolumn was minimized. The length of the tubing used was 167 mm to the injection valve and 315 mm to the nebulizer inlet.

The alumina column was acidified by flowing 0.01 M of nitric acid through it at a rate of 1.6 ml min^{-1}. During preconcentration the flow rate was increased to 5 ml min^{-1} in order to increase the sample adsorption rate. The adsorbed molybdate was eluted by the injection of 0.25 ml of ammonia solution (2 M). The preconcentrated sample was introduced into the ICP directly.

When sea water was analyzed during initial experiments, high dissolved salts were deposited on the tip of the central tube of the ICP torch. To overcome this problem, the sample which passed through the column during preconcentration was discarded into a drain (see Fig.1).

2.2. ICP operating conditions

With the observation height set at 20 mm above the load coil, plasma power and carrier-gas flow rate were optimized for the emission of molybdenum ion. Precise optimization procedures are described elsewhere [6]. RF power was operated at 1.9 kW and the optimal outer, intermediate, and inner argon-gas flow rates were found to be 16.0, 0.5, and 0.9 l min^{-1}, respectively. A glass concentric nebulizer was used and a sample uptake rate of 1.6 ml min^{-1} was maintained with the use of a peristaltic pump.

2.3. Spectrally segmented photodiode-array spectrometer

A PLASMARRAY (LECO® Corporation) spectrometer was used in this study. The unique features of the instrument have been described in detail elsewhere [7,8] and the optical arrangement will be described here only briefly. In this spectrometer, three gratings are employed for dispersion and a linear photodiode array (1024 channels) is used as a detector. The ICP emission is initially passed through a low dispersion polychromator. At the exit port of this polychromator a demountable, slotted mask is located whose slots can be set to pass desired light and block unwanted wavelengths. The segmented light which passes through the slots is collimated by a second grating which undoes the original dispersion and produces pseudo-white-light beam. At the final stage, the pseudo-white light is dispersed by an Echelle grating operated at high order and high resolution. Because the instrument has no dispersion function along the vertical direction, the segmented spectra of different orders are superimposed and observed simultaneously by the linear photodiode-array detector.

In this paper, a mask constructed specifically for molybdenum was used to select several analytical lines. This is the same mask used to obtain detection limits for 10 molybdenum lines in another paper [6]. The entrance slit of the pre-polychromator was set at 25 μm, and the position was adjusted to optimize the emission lines. Out of these lines the most sensitive three lines were selected for analysis (Mo II 287.151 nm, Mo II 281.615 nm, and Mo II 277.540 nm). Therefore, only spectral information obtained from channel range 140 - 340 was used, even though the photodiode array has 1024 channels. The reciprocal linear dispersion in this wavelength region is 0.078 nm mm^{-1} and the resolution at full width at half maximum is 0.006 nm.

2.4. Analytical procedures

The time required for complete transfer of a sample loaded onto the sample-loop (0.25 ml) was 50 seconds. Therefore, the transient emission signal observed during the elution of an adsorbed molybdate sample was integrated on the photodiode array detector for 50 seconds. Regardless of the amount of molybdate adsorbed on the alumina column, 87 % of the total molybdate was eluted by one injection of ammonia. Therefore, between samples it was necessary to clean the alumina column by repeating the elution step several times. After thus cleaning the column, a blank spectrum was obtained while nitric acid (0.01 M) was flowing continuously into the ICP. Immediately prior to each analysis, a new blank spectrum was obtained for each sample.

The blank-subtracted spectra were initially stored and recalled for processing after the completion of data collection. A baseline was obtained from three pixels chosen from both sides of the emission peak and a regression line was drawn through them. Five pixels, centered on the analytical line of interest, were used to calculate the area of the spectral peak above the regression line [6].

2.5. Reagents and materials

A molybdenum standard solution of 1000 $\mu g\ ml^{-1}$ was purchased from Aldrich Chemical Company, Inc. The solution was prepared by dissolving $(NH_4)_6Mo_7O_{24}$ in water. The standard solution was appropriately diluted with distilled and deionized water (pH4) and stored in precleaned polypropylene containers (Nalgene). The activated alumina used for column preparation was Brockman Activity 1 produced by Fisher Scientific. Nitric acid, ammonium hydroxide and sodium chloride were obtained from Mallinckrodt, Inc. All of the chemicals were analytical reagent grade and were used without further purification. Standard sea water, NASS-2, (molybdenum concentration: 11.5 ± 1.9 ng ml^{-1}) was obtained from the National Research Council in Canada.

3. RESULTS AND DISCUSSION

3.1. Linearity and detection limits

In order to check the linearity of the technique, standard solutions of molybdenum ranging from 100 to 1000 ng ml^{-1} were preconcentrated for 1 min on the alumina column and eluted by 0.25 ml of ammonia solution. Since 5 ml of the sample was used during the one-minute preconcentration period, it is calculated that the preconcentration factor is approximately 20. As shown in Fig. 2, the integrated spectral-peak area exhibits good linearity with molybdenum concentration.

With increasing preconcentration time more emission intensity can be expected from the same initial sample concentration. To test this feature, a molybdenum standard solution of 100 ng ml^{-1} was preconcentrated over time periods ranging from 1 min to 10 min (Fig 3). The peak area increased linearly with preconcentration time. Of course, when the preconcentration time ranges between 1, 3, 5, and 10 min, the required sample volume also increases as 5, 15, 25, and 50 ml, respectively. Since the volume of ammonia that is used to elute the preconcentrated molybdenum is constant (0.25 ml), the preconcentration factor is increased proportionately. For the example given above, preconcentration factors increase as 20, 60, 100, and 200, respectively. By extending the preconcentration time from 1 to 10 min, the technique can be applied readily to molybdenum standard solutions having concentrations between 10 - 100 ng ml^{-1}. As shown in Fig. 4, a calibration curve similar to that shown in Fig. 2 was obtained for concentrations one order of magnitude lower. The fact that all calibration curves presented in Figs 2-4 are almost equivalent supports the fact that the emission intensity is dependent only on the total amount of molybdenum deposited on the alumina column, regardless of either the initial sample concentration or the preconcentration time.

Following the method and argument described elsewhere [6], detection limits for molybdenum were obtained as the concentration which produces a signal equal to three times the standard deviation of the side-band background noise multiplied by $\sqrt{5}$. These detection limits are listed in Table 1 along with those obtained by continuous-nebulization modes. Because of preconcentration, the detection limits obtained here are better than those achieved using continuous-nebulization techniques by a factor of approximately 50. In order to illustrate this improvement, the emission spectrum obtained from a preconcentrated molybdenum solution of 50 ng ml^{-1} is compared in Fig.5 with that obtained for the same solution by the continuous-nebulization mode.

3.2. Spectral background

When the preconcentration flow-injection technique was applied to solutions having a low concentration of molybdenum, a shift in the ICP background was observed when the ammonia solution was used to elute the adsorbed molybdate. Figure 6(a) reveals the background shift observed when a molybdenum solution of 10 ng ml^{-1} was measured after a 10-minute preconcentration. This shift corresponds to about 7 % of the total ICP background. The same background shift was observed when the alumina column was removed and 0.25 ml of ammonia solution was injected. This behavior is illustrated in the upper spectrum of Fig. 6(b). After replacing the alumina column, a blank-subtracted spectrum was obtained without ammonia injection using the same blank spectrum. As shown in the lower spectrum of Fig. 6(b), the blank-subtracted spectrum was flat if the ammonia solution was not injected. Apparently, the observed background shift is a result of the temporary change in plasma conditions caused by the injection of ammonia. Importantly, when the emission intensity is monitored at a single wavelength by a photomultiplier-based detection system, the extent of this background shift cannot be determined and an error occurs in the analytical results. In contrast, when the spectrum is monitored by a photodiode array detector, the background shift can be corrected easily.

3.3. pH response

In order to evaluate the pH response of the alumina preconcentrating column, the pH of initial molybdenum solutions were adjusted by nitric acid or ammonium hydroxide and the preconcentration flow-injection analysis then carried out. The results are presented in Fig. 7. When the pH of the sample solution was less than 2 or more than 4, a fraction of the molybdenum broke through the column. Therefore, the pH of the sample should be adjusted between 2 and 4 prior to analysis.

3.4. Matrix interferences

Taking the application of sea water into consideration, the effect of high concentrations of dissolved sodium chloride was determined. Molybdenum solutions of 50 ng ml^{-1} were measured in the presence of sodium chloride at concentration levels of 0.1, 0.3, 0.5, 1.0, 2.0, and 3.0 %. Surprisingly, as seen in Fig. 8, such high concentrations of sodium chloride did not affect significantly the performance of the alumina column.

3.5. Precision

Ten measurements were repeated and the precision was expressed as the relative standard deviation of the resulting spectral peak areas. The results are summarized in Table 2. As a typical case for high concentrations, a molybdenum solution of 500 ng ml^{-1} was measured after a 1-min preconcentration. About 2 % relative standard deviation was obtained. To represent low concentrations, a molybdenum solution of 10 ng ml^{-1} was measured after a 10-min preconcentration. The relative standard deviation at this concentration level was about 5 %.

3.6. The determination of molybdenum in a standard sea-water sample

The standard sea-water sample (NASS-2) was collected at the 1300 meter level, southeast of Bermuda. Immediately after collection, the sea water was acidified to pH 1.6 with nitric acid and stored in a polyethylene bottle.

Prior to analysis, the pH of the standard solution was adjusted to pH 3 with ammonium hydroxide. The sample was then measured using a 10-min preconcentration period. A typical resulting spectrum is shown in Fig. 9. When this spectrum is compared with the one in Fig. 6(a), a suppression effect is noted for the sea-water standard. The origin of this suppression effect was not investigated here thoroughly. Instead, to overcome the effect of the observed suppression, the standard-addition method was employed. By adding known amounts of molybdenum in sea water, the flow-injection procedure was conducted after a 10-min preconcentration. The spectral-peak areas for three analytical lines are plotted in Fig. 10 and the extrapolated analytical results are summarized in Table 3. Excellent agreement of the determined and certified values attests to the accuracy of the developed method.

4. CONCLUSION

The use of an alumina column was shown to be a very efficient method for preconcentrating molybdenum in an aqueous sample. Combination of the alumina column and flow-injection analysis is a very simple but very powerful technique, which can be used when the sample concentration is too low or the sample matrix is too complex for an available instrument. The determination of molybdenum in sea water was a good example of such an instance.

Flow-injection analysis incorporating the acidic alumina column could be applied to the determination of other oxyanions such as arsenate, borate, chromate, phosphate, selenate, sulphate, tungstate, and vanadate. Since the sensitivity of ICP-AES is relatively low for these elements, the simple preconcentration technique described in this paper might be a useful method. However, when such a low concentration of oxyanions is measured by preconcentration flow-injection analysis, a background shift occurs that is caused by the injection of ammonia. If the emission signal were monitored at a single wavelength by a photomultiplier-based measurement system, the extent of this background shift would not be observed. In contrast, the photodiode-array-based detection system used in this study is capable of correcting for such a transient background change. This is one of the biggest advantages of this photodiode-array-based detection system.

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Table 1. Detection limits$^{a)}$ (ng/ml)

	Wavelength (nm)	Preconcentration FIA$^{b)}$, this study	Continuous nebulization$^{c)}$
Mo II	287.151	0.22	12
Mo II	281.615	0.21	8
Mo II	277.540	0.34	16

a) See text for definition

b) A *10-min preconcentration was used.*

c) Cited from Ref. [6]. Integration time was 50 s and 5 pixels, centered on the emission peak, was used to obtain area of spectral peak.

Table 2. Precision[a] (%R.S.D.)

	Wavelength (nm)	500 ng ml^{-1} Mo 1 min preconcentration	10 ng ml^{-1} Mo 10 min preconcentration
Mo II	287.151	1.95	4.99
Mo II	281.615	2.17	5.55
Mo II	277.540	1.97	4.50

a) Relative standard deviation calculated from 10 determinations.

Table 3. Analytical results of sea water, NASS-2

	Wavelength (nm)	Mo concentration found (ng/ml)	Certified value (ng/ml)
Mo II	287.151	9.7	
Mo II	281.615	10.6	
Mo II	277.540	10.5	
	average	10.3 ± 1.0[a)]	11.5 ± 1.9[a)]

a) The uncertainties represent 95.5 % tolerance limits.

FIGURE CAPTIONS

Fig. 1. Schematic diagram of the preconcentration flow-injection system.

Fig. 2. Area of Mo II spectral peak as a function of molybdenum concentration (1 min preconcentration).

○: Mo II 287.151 nm, Best fit line: $Y = 5.70X + 43.7$ $R^2 = 0.999$

Δ: Mo II 281.615 nm, Best fit line: $Y = 4.25X - 15.4$ $R^2 = 1.000$

□: Mo II 277.540 nm, Best fit line: $Y = 2.83X - 19.7$ $R^2 = 1.000$

Fig. 3. Area of Mo II spectral peak as a function of preconcentration time (100 ng ml^{-1} Mo).

○: Mo II 287.151 nm, Best fit line: $Y = 562X + 86.2$ $R^2 = 1.000$

Δ: Mo II 281.615 nm, Best fit line: $Y = 377X + 81.2$ $R^2 = 1.000$

□: Mo II 277.540 nm, Best fit line: $Y = 251X + 42.6$ $R^2 = 1.000$

Fig. 4. Area of Mo II spectral peak as a function of molybdenum concentration (10 min preconcentration).

○: Mo II 287.151 nm, Best fit line: $Y = 56.7X - 14.2$ $R^2 = 1.000$

Δ: Mo II 281.615 nm, Best fit line: $Y = 38.0X + 53.6$ $R^2 = 1.000$

□: Mo II 277.540 nm, Best fit line: $Y = 25.3X + 26.2$ $R^2 = 1.000$

Fig. 5. Comparison of spectra obtained by

(a) preconcentration flow-injection analysis
(50 ng ml^{-1} Mo, 10 min preconcentration) and

(b) continuous-nebulization mode (50 ng ml^{-1} Mo).

Fig. 6. (a) Preconcentration flow-injection analysis
(10 ng ml^{-1} Mo, 10 min preconcentration).

(b) Spectral background observed during flow-injection analysis
upper: without an alumina column, but with ammonia injection
lower: with an alumina column, but without ammonia injection.

Fig. 7. Effect of pH of molybdenum solution that are being preconcentrated on the alumina column (500 ng ml^{-1} Mo, 1 min preconcentration).

○: Mo II 287.151 nm, Δ: Mo II 281.615 nm, □: Mo II 277.540 nm.

Fig. 8. Interference effect of sodium chloride on preconcentration flow-injection analysis of molybdenum (50 ng ml^{-1} Mo, 10 min preconcentration).

○: Mo II 287.151 nm, Δ: Mo II 281.615 nm, □: Mo II 277.540 nm.

Fig. 9. Molybdenum emission spectrum of preconcentrated sea-water standard, NASS-2, (10 min preconcentration). The concentration of molybdenum in the original standard solution is certified to be 11.5 ± 1.9 ng ml^{-1}.

Fig. 10. Determination of molybdenum in sea water by the standard-addition method

○: Mo II 287.151 nm, Best fit line: $Y = 35.1X + 341$ $R^2 = 0.986$
Δ: Mo II 281.615 nm, Best fit line: $Y = 23.7X + 252$ $R^2 = 0.982$
□: Mo II 277.540 nm, Best fit line: $Y = 16.0X + 167$ $R^2 = 0.987$

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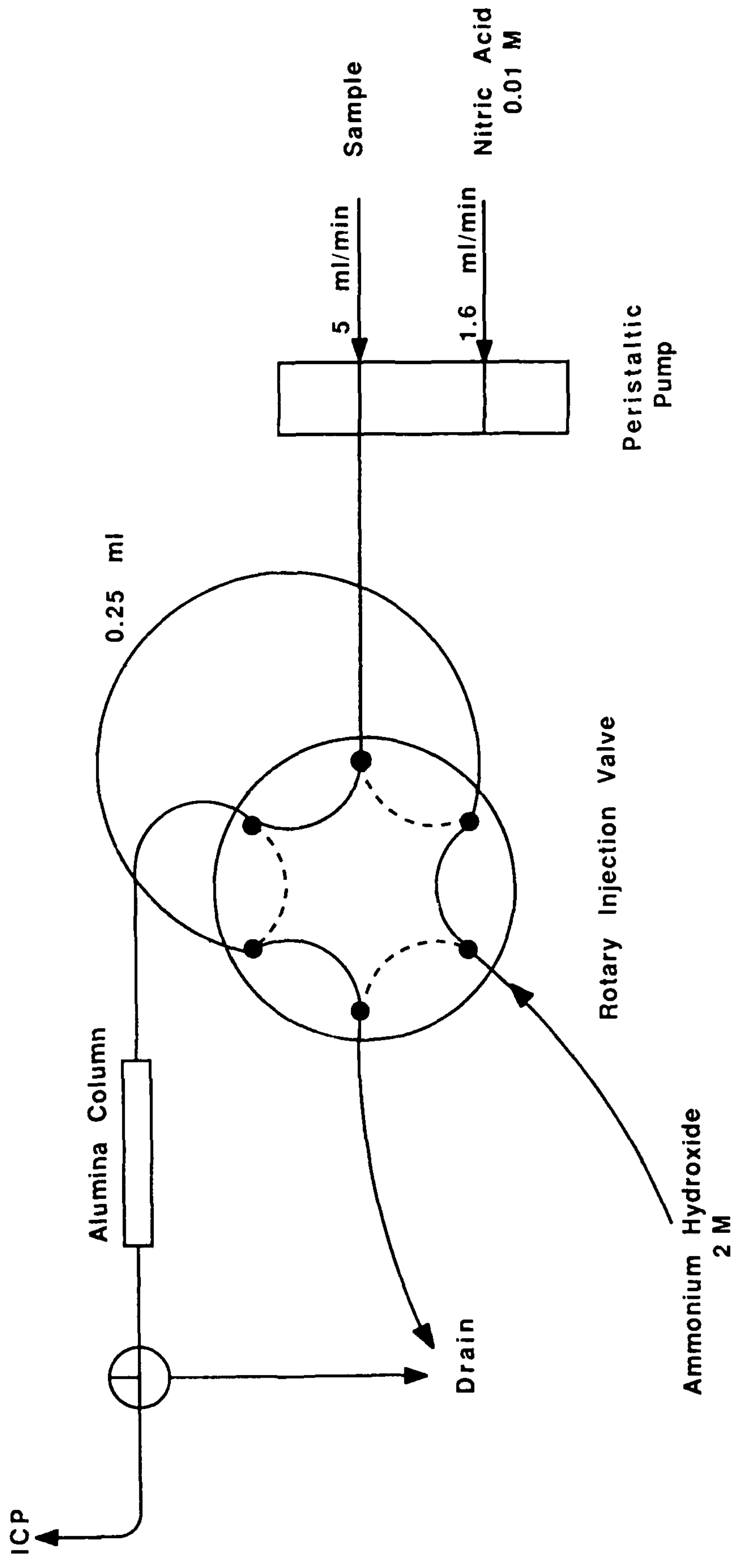

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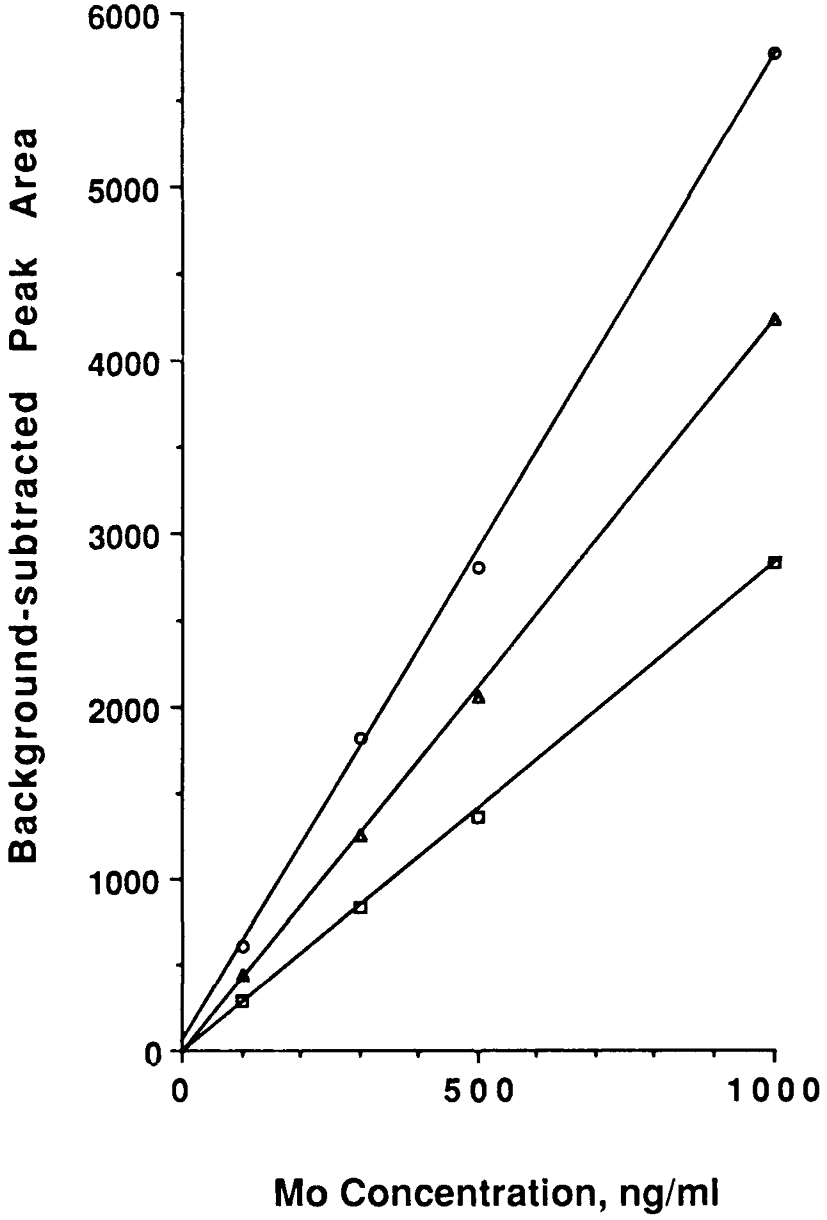

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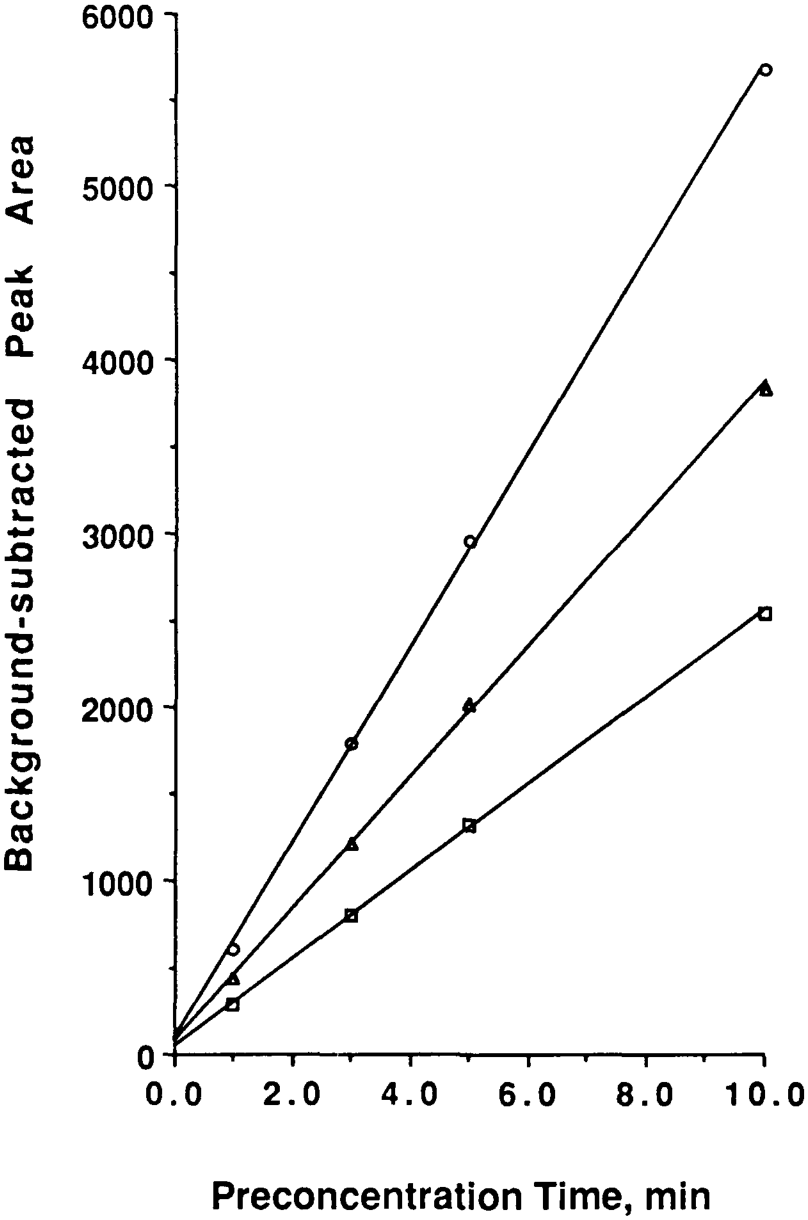

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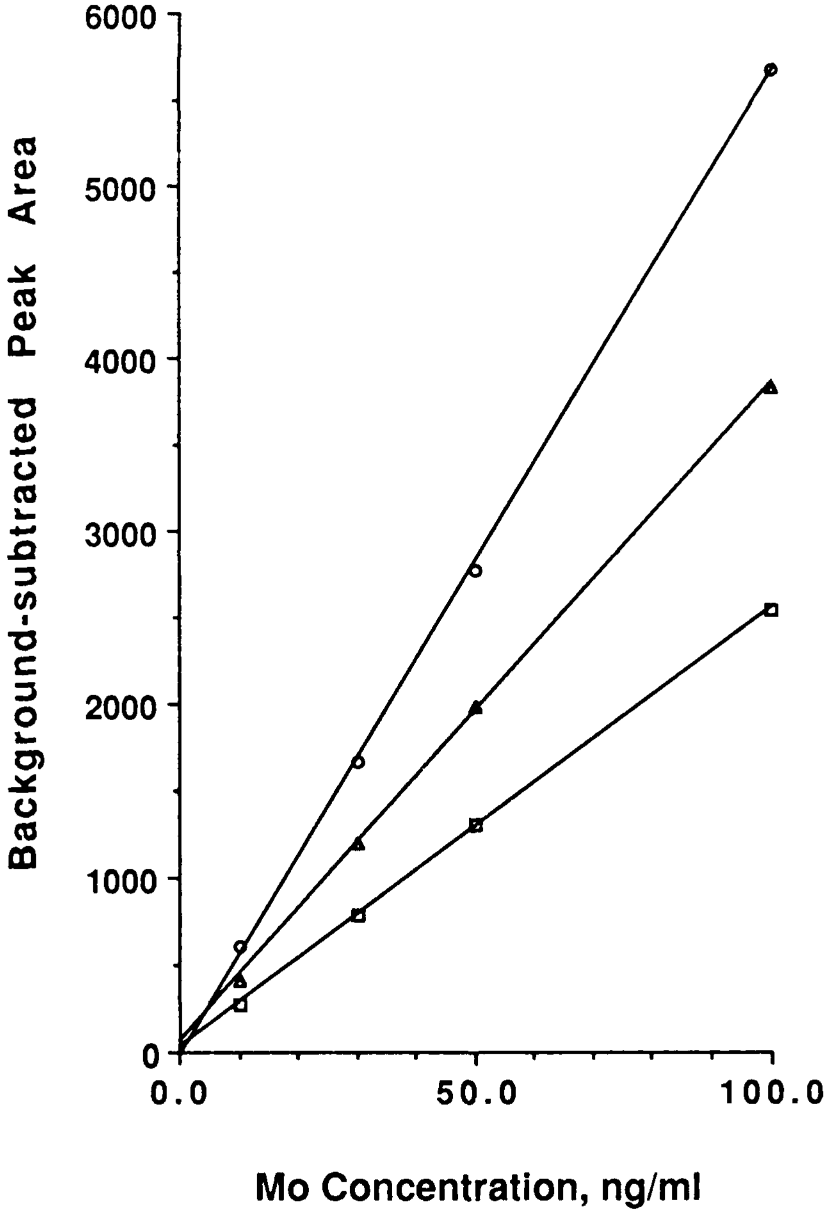

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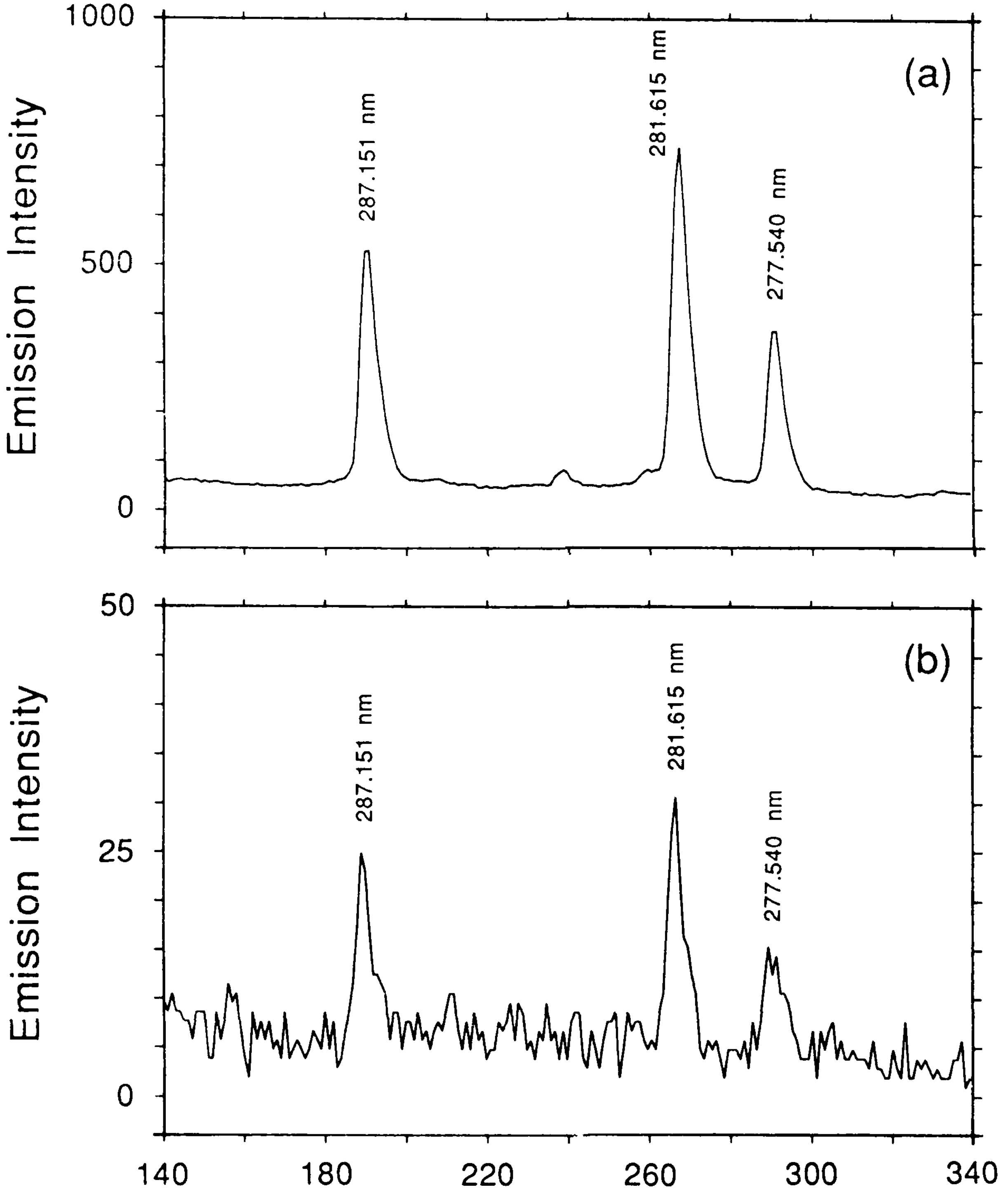

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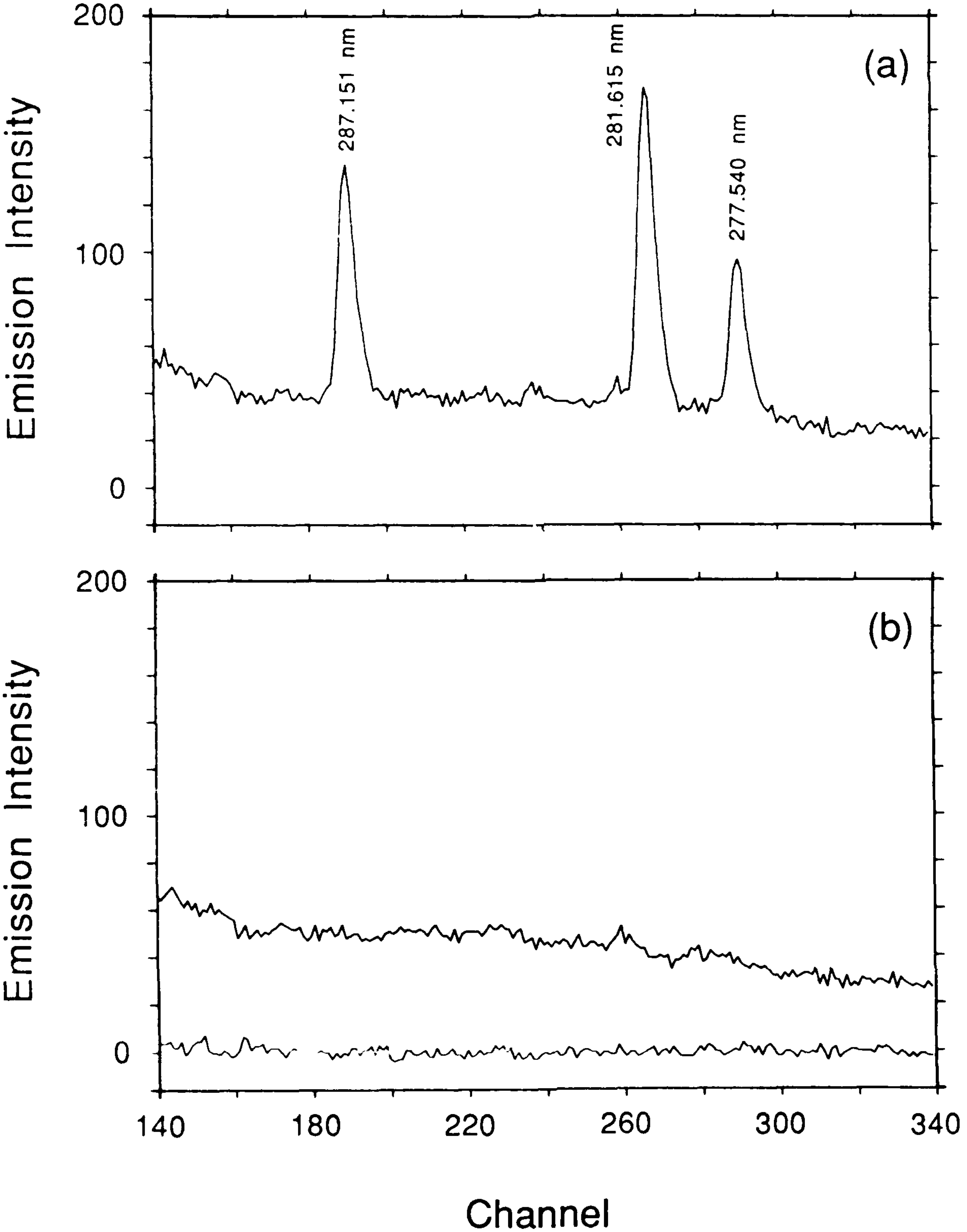

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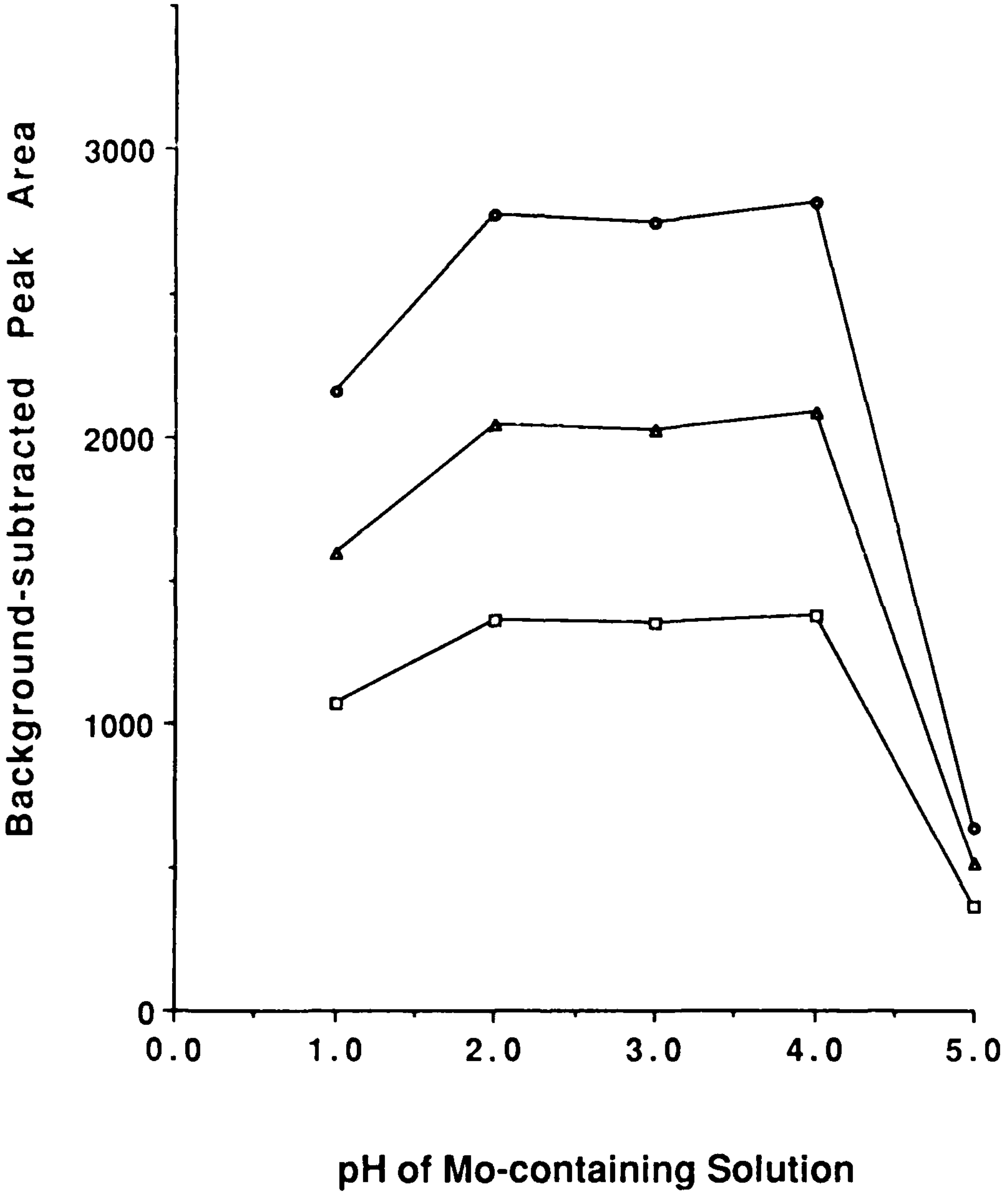

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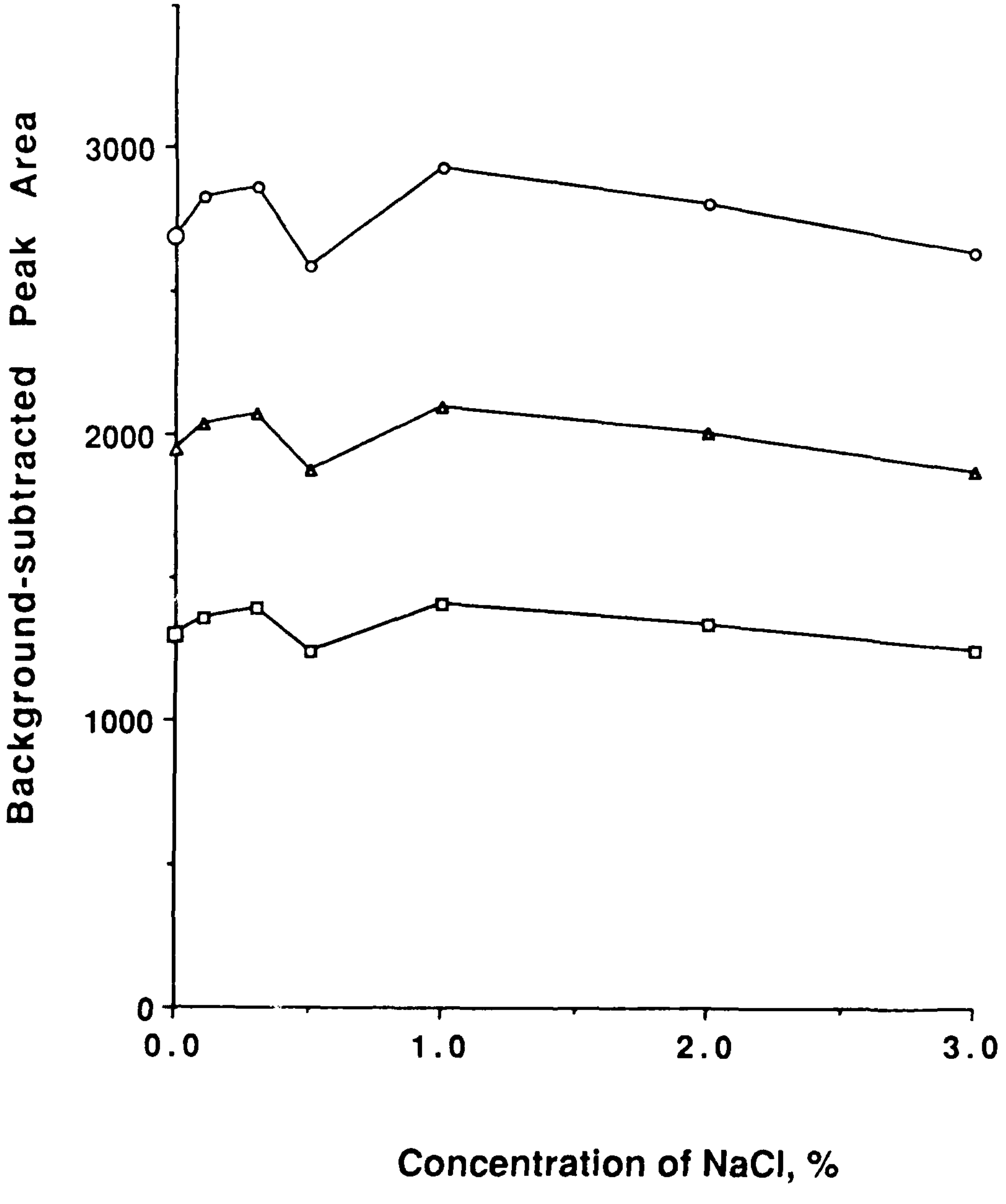

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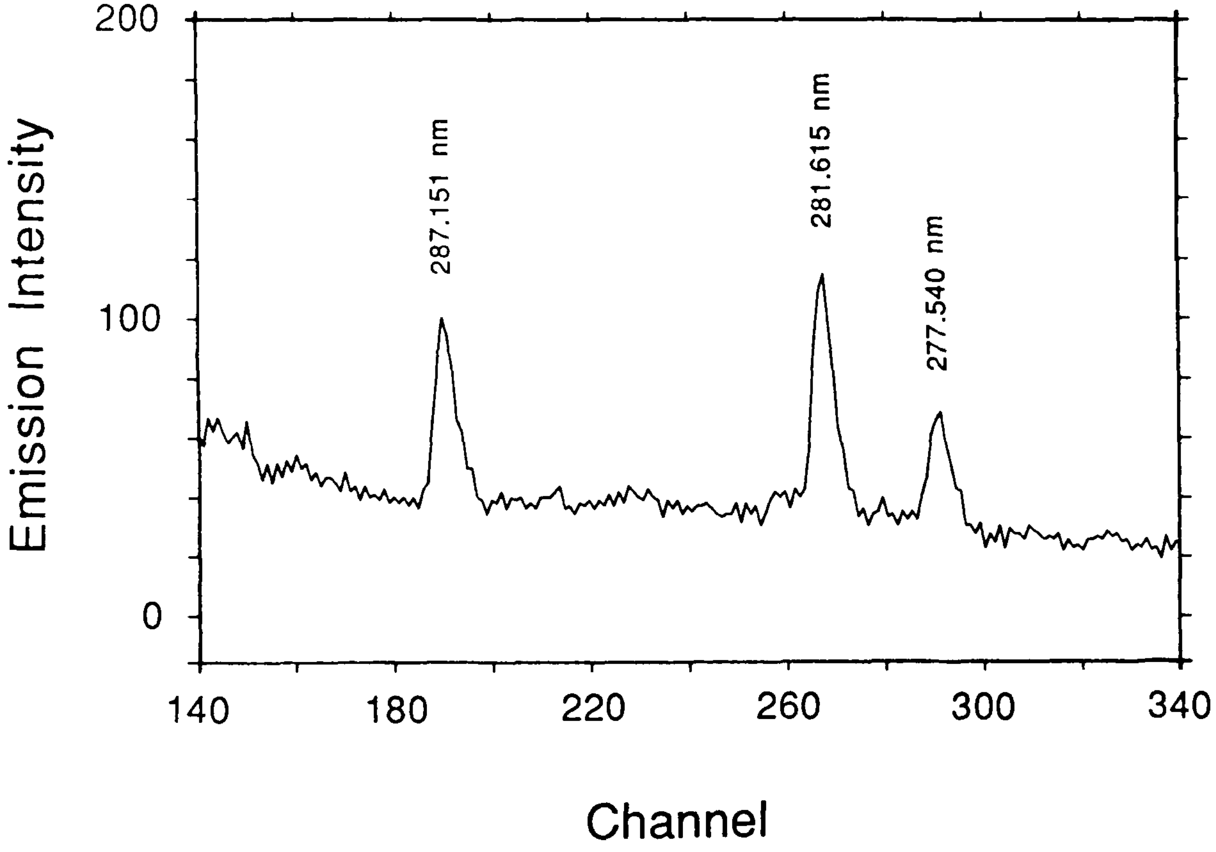

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