

A Novel Method for the Measurement of Strontium in Water Samples

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Abstract:

With this student project, we were able to develop a new method for measuring strontium (Sr) ion concentration, to part per million level in environmental water samples that has never been reported in the literature. In this project, develop a new method for the detection of Sr in the water exposed to the sediment using fluorescence of a Sr complex was developed. Fluorescence methods have been used in environmental analysis to measure part per million levels of organic residues in aqueous systems, such as pesticides in stream water, but not for metals ions. The development of a fluorescence method for strontium offers the potential for a field analysis method with portable fluorimeters. Another benefit is that it offers a route for testing that employs non-radioactive forms of strontium, making it safer for personnel and the environment. Strontium can be quantitatively extracted from an aqueous solution at pH greater than 11.5 by a 0.5M oxime solution in chloroform. The complex formula (strontium oxinate) is $\text{SrL}_2(\text{HL})_2$, where L = 8-hydroxyquinoline or oxime. Any interfering ions can be removed with a preliminary extraction as oxinates at a lower pH. When an excitation wavelength of 392 nm was used, the emission of the standard solutions obeyed the linear equation: $E = K_\lambda C + b$ in the region of 485 nm to 520 nm with r values close to 1.00 in all cases. In addition, at the emission peak at 392 nm for concentrations 30 ppm and below also show linear correlation of emission with concentration. To simulate an aquatic environment, sediment from a nearby stream was placed in plastic containers. In one of the tanks, the water and sediment was stirred daily, while in the other the water and sediment were left undisturbed. After 5 days samples were removed and analyzed. The results of measured strontium levels, using the fluorescence, showed that the free Sr concentration in each sample was decreased from the starting concentration, indicating the ion was adsorbed onto the sediment. About 40% of the original concentration was adsorbed in the standing tank, whereas 67% (or two-thirds) was adsorbed in the tank stirred once a day for 5 days. These results are consistent with the number and surface of the particles in the sediment exposed determining the extent of Sr adsorption. The implication of these results is that any concentration of Sr detected in stream water will be less than half than present in the sediment. The greater the stream sediment is disturbed by spring run-off or heavy rainstorms, the greater the difference between the ambient stream concentration and that in the sediment of the Sr from the stream water.

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With this student project, we were able to develop a new method for measuring strontium (Sr) ion concentration, to the part per million level in environmental water samples that has never been reported in the literature. In the original project, we had planned to study kinetics of Sr uptake with a typical sediment sample from one of the creeks around West Valley. However, the agencies involved (DOE, NYSERDA) decided that no sediment from anywhere on the 3000 acre site could be removed due to agency policy. Then the project evolved into studying Sr adsorption in a simulated environment, using a sediment from nearby creek, which shared some geologic similarities with sediment at West Valley. Due to the lateness of funding, the experiments concentrated on trials with one type of sediment. The focus of the experiments then also became whether we could develop a new method for the detection of Sr in the water exposed to the sediment using fluorescence of a Sr complex. Fluorescence methods have been used in environmental analysis to measure part per million levels of organic residues in aqueous systems, such as pesticides in stream water. They also are used to detect low levels of certain metals in aqueous biological samples, such as in cellular transport of calcium ions. As a technique, it is a very selective, precise and reproducible method which does not require extensive pretreatment of the sample. In addition, the development of a fluorescence method for strontium offers the potential for a field analysis method with portable fluorimeters. Another benefit is that it offers a route for testing that employs non-radioactive forms of strontium, making it safer for personnel and the environment.

Spectroscopic methods are preferred type of analysis since they are very sensitive and reproducible measures of concentration. As is characteristic of most alkaline earth metals, strontium is difficult to measure with spectrophotometry because it does not form colored complexes with organic or inorganic substances. Atomic absorption methods are typically used to detect metal ions in very low concentration. When coupled with ion-coupled plasma (ICP) analysis, it is the standard method for detection of Sr in water samples. Although very sensitive, these methods cannot be developed into a direct field measurements, since the instrument required would not lend itself to a portable design. In contrast, a fluorescence method does not require colored complexes, so it can be applied to alkaline earth elements, and has the potential to be developed into a field method. An extensive review of the literature showed fluorescent measurements are commonly used for calcium, but that strontium methods had not been developed. Older references indicated that Sr could be produce fluorescence if complexed with reagents such as 8-hydroxyquinoline (1-2), but little, if any, of the experimental parameters had been determined. The compound, 8-hydroxyquinoline or "oxime" forms rigid complexes with alkaline earth and some transition metals, in nonpolar solvents, which produce the conjugated systems required for fluorescence. A method used to prepare and then extract the strontium-oxime complex into chloroform was first published in 1964 (3) and was adapted for the fluorescence analysis in this experiment. The fluorescence of the complex in chloroform was measured using a scanning fluorescence spectrophotometer to

determine the excitation and fluorescence wavelengths. A detailed description of the extraction procedure appears in the experimental section below. Figure 1 shows a typical fluorescence spectrum obtained for the complex (corrected for the absorption of uncomplexed oxime in chloroform as the background). The two peaks observed in the spectrum are consistent with that expected for fluorescence. The first peak near the wavelength absorbed (excitation wavelength) is very strong and is caused by re-emission of the absorbed energy (excited state to ground state energy transition). This is followed by peak(s) at longer wavelength (lower energy) which represent the singlet transition(s) of the excited state electrons to higher vibrational states within the ground state, typical of fluorescence. That the lower energy transitions appear as a band for this complex, is probably indicative of solvent effects on the transitions.

Analysis of standard solutions of strontium nitrate in water produced the plot represented in Figure 2. The emission of the standard solutions obeyed the linear equation: $E = K_{\lambda}C + b$ in the region of 485 nm to 520 nm (Figure 3 and Table 1) where E equals the emission intensity (in arbitrary units), K_{λ} a collection of constants specific to the wavelength, and C the concentration of Sr. The maximum wavelength shifts slightly with concentration in this range, but does so in a linear fashion (Figure 4). This is consistent with the quantum yield for a particular transition being affected by concentration. However, the slopes of the concentration versus emissions lines all show strong linear correlations with r values close to 1.00 in all cases. In addition, the emission peak at 392 nm for concentrations 30 ppm and below also show linear correlation of emission with concentration (Figure 5).

Analysis of the standards also indicated that lower limit for the Sr-oxime concentration detectable by peaks in the 485-520 nm range is 10 ppm. Values of concentration as high as 100 ppm Sr show deviation from the linear behavior at these wavelengths, consistent with either self-absorption or self-quenching effects. It therefore appears that 50 ppm is probably a good working upper limit concentration that can be precisely detected by this method. However, the emissions at 392 nm are much stronger and working limit may be extended much lower to less than 1 ppm, at this wavelength whereas the maximum appears to be 30 ppm Sr. Portable, inexpensive fluorimeters are currently available with the needed excitation wavelength range needed for the Sr-oxime complex, as well as the capability to measure the fluoresced wavelengths, so that field measurement instrumentation would be available.

To simulate an aquatic environment, sediment from a nearby stream was placed in two plastic containers with 8.0L of solution containing the same concentration of strontium nitrate (ACS reagent grade), as described below in the experimental method section. The literature concerning strontium uptake indicated that Sr is strongly adsorbed by sediment particles in streams and that the process is strongly dependent on the size of the exposed surface and number of the particles (4-5). To see whether we could detect a difference in concentration based on sediment exposure, in one of the tanks, the water and sediment was stirred daily, while in the other the water and sediment were left undisturbed. After 5 days, which, according to the literature (6) should have been sufficient time for the adsorption to equilibrate, samples

were removed and analyzed. The results of measured strontium levels, using the fluorescence appear below in Tables 2 and 3. The free Sr concentration in each sample was decreased from the starting concentration, indicating the ion was adsorbed onto the sediment. About 40% of the original concentration was adsorbed in the standing tank, whereas 67% (or two-thirds) was adsorbed in the tank stirred once a day for 5 days. These results are consistent with the number and surface of the particles in the sediment exposed determining the extent of Sr adsorption. The implication of these results is that any concentration of Sr detected in stream water will be less than half than present in the sediment. The greater the stream sediment is disturbed by spring run-off or heavy rainstorms, the greater the difference between the ambient stream concentration and that in the sediment of the Sr from the stream water.

In conclusion, the new method has proved itself capable of determining the Sr concentration in water, in the presence of other ions and has produced results consistent with the published data. A future experiment will be to determine if the Sr can be extracted from the sediment using the oxime reagent method and measured with fluorescence. This method could then prove to be useful to determine the stored concentration of Sr in the sediment. In addition, further experimentation can be conducted with other types of extracting or chelating agents, known to produce fluorescence with calcium, to determine their sensitivity to Sr. This would address the potential disadvantage of an extraction procedure with a field method. Ideally, the fluorescence determination of a water soluble complex with Sr would be very advantageous for the development of this method into an, easy reproducible field method.

Experimental Method:

Extraction Procedure:

Strontium can be quantitatively extracted from an aqueous solution at pH greater than 11.5 by a 0.5M oxime solution in chloroform. The complex formula (strontium oxinate) is $SrL_2(HL)_2$ where L = oxime. Any interfering ions can be removed with a preliminary extraction as oxinates at a lower pH. (0.1 M oxime in chloroform used for preliminary extraction). The pH of the sample solutions is adjusted to 9.0 and interfering ions extracted with successive portions of 0.10M oxime until the organic phase is colorless. (The oxinate complexes are typically yellow, but a few are greenish colored). Any Sr in the solution will not be extracted at pH = 9.0. Adding an ammonia solution (6.0 M) dropwise to the sample solution should be used to bring pH to 9.0.

After this preliminary extraction, add 0.10M NaOH to bring the pH to 11.5-12.0. (measure with pH strip or if using a pH electrode be careful not to leave in the solution very long.) Extract Sr with an equal volumes (20 mL) of 0.50M oxime in chloroform and aqueous solution in a separatory funnel, The extraction occurs rapidly, so only need about 1 minute of shaking of the funnel. Place the extract in a clean, dry 100 mL Erlenmeyer flask. Repeat the extraction a second time. Combine the organic extracts, mix and then measure absorbance and emission of the sample. The uncomplexed oxime absorbs at 318 nm. The chelate absorbs

380-400 nm so an excitation wavelength of 390 nm should be used. Note: The oxime solutions are light sensitive and should be stored in a brown bottle.

Sample Treatment:

Sediment samples were taken from Ellicott Creek from a spot of standing water near the bank. Then two tanks were set up as standing water, with sediment in the bottom. One of the two tanks has a starting concentration of 200ppm Sr in 8 liters of water. All tanks have 8 liters of water. The other tank is basically identical to the first, except that it gets stirred once a day. Twenty milliliter samples were removed from the tanks and refrigerated until they could be analyzed. The instrument used was the Cary Eclipse Fluorescent Spectrophotometer from Varian. The default settings for the software were adjusted to find the excitation wavelength by setting the emission reading to zero, and having the spectrophotometer scan from 200 to 700 nm. The excitation wavelength was the determined from the scan. Then the instrument was set it to run overlay graphs and performed emission scans with an excitation wavelength at 392 nm. The background sample was made by using the extraction procedure given above on distilled water. Then the emission scan from 200 to 700 nm for each standard and sample solution was measured. The spectrum with the extract from the distilled water was subtracted from the scans as the background using the software in the computer. The samples from the tank was diluted by a factor of 1:4 so that it's initial concentration was diluted to 50ppm before it was analyzed.

Figures and Data:

Figure 1: A typical spectrum of the extracted Strontium-oxime complex, corrected for background absorption.

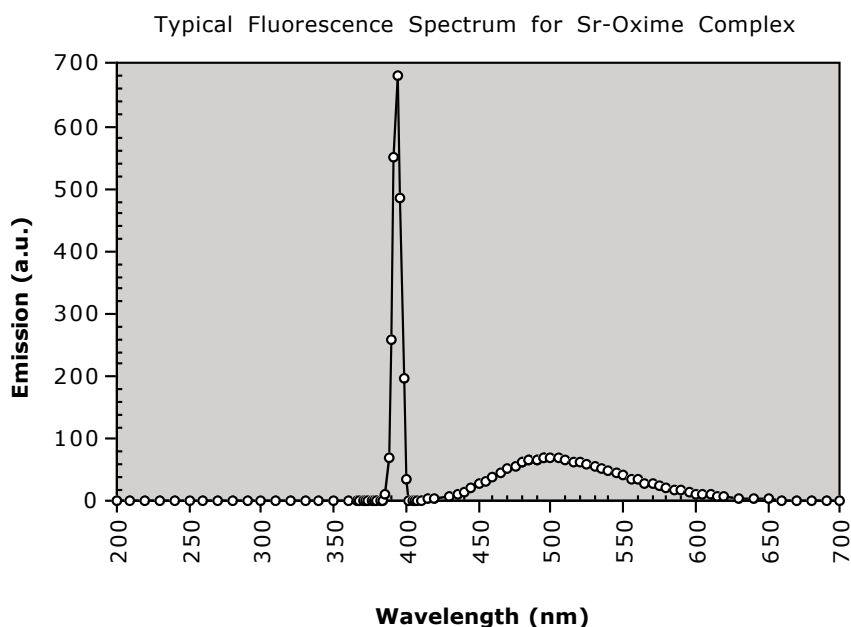


Figure 2: Overlay of standard spectrum of the extracted Sr-oxime complex

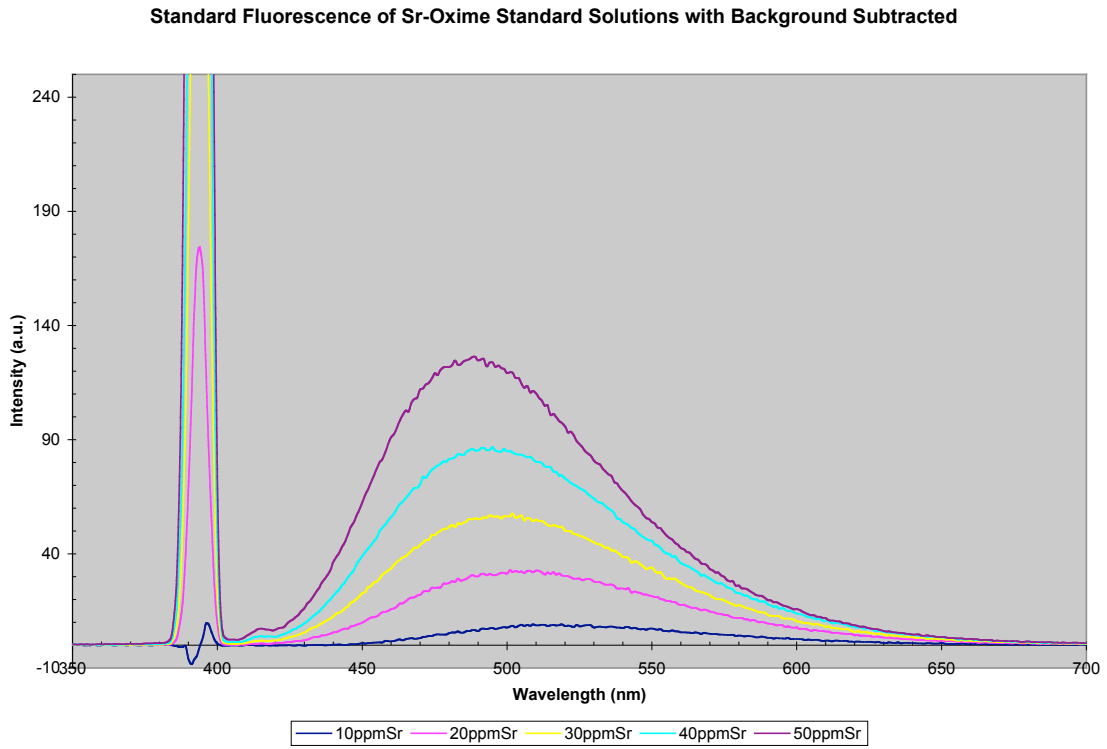


Figure 3: Plot of Standard Concentration versus Emission at Different Wavelengths

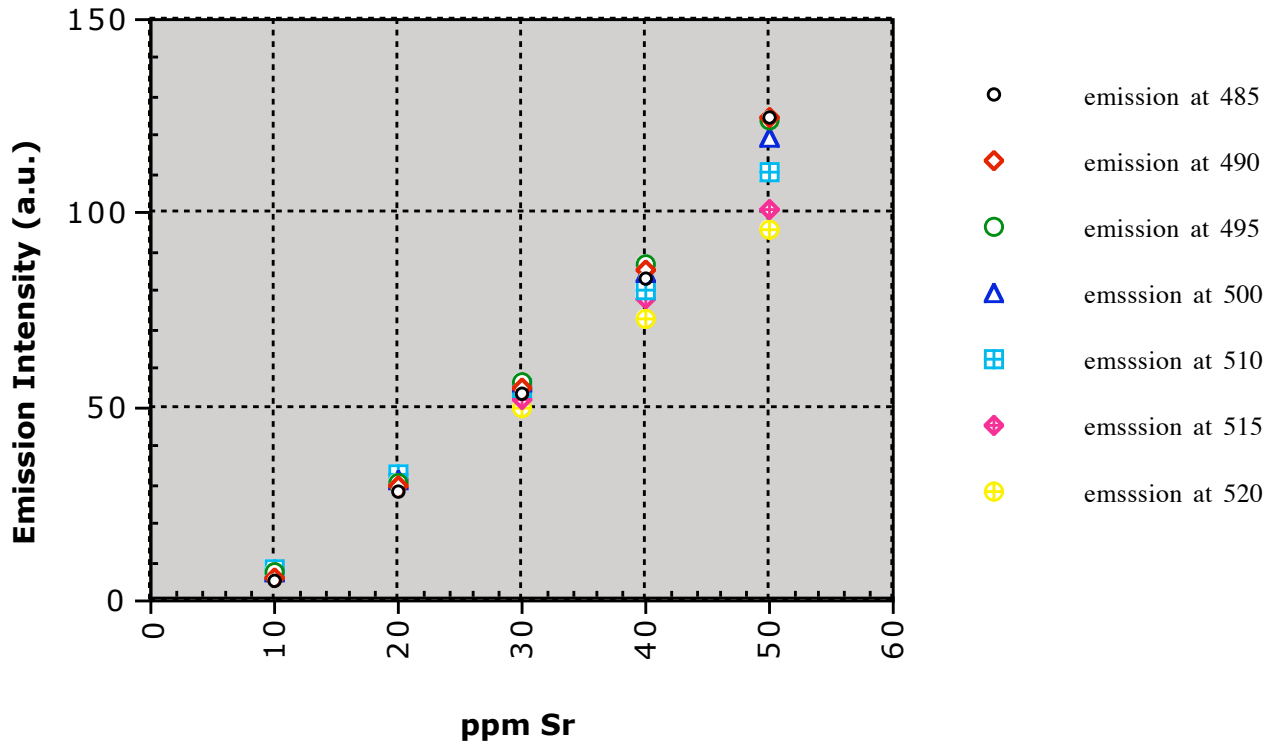


Table 1: Linear regression analysis of standard curves for Sr-oxime complex

Wavelength (nm)	slope, K_1	y-int	Correlation coefficient, r
485	2.922	-28.564	0.9930
490	2.924	-27.423	0.9940
495	2.883	-25.473	0.9950
500	2.765	-23.011	0.9970
510	2.508	-17.859	0.9980
515	2.311	-15.151	1.0000
520	2.176	-13.775	1.0000

Figure 4: Plot of emission versus concentration of standard solutions at 392 nm.

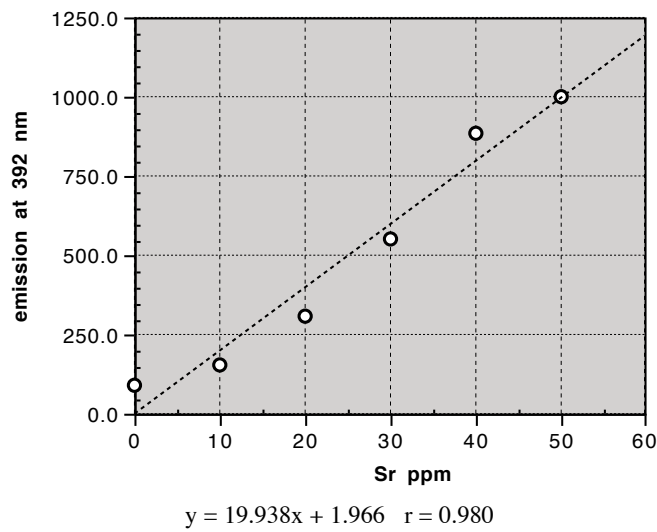


Figure 5: Lambda maximum variation with concentration

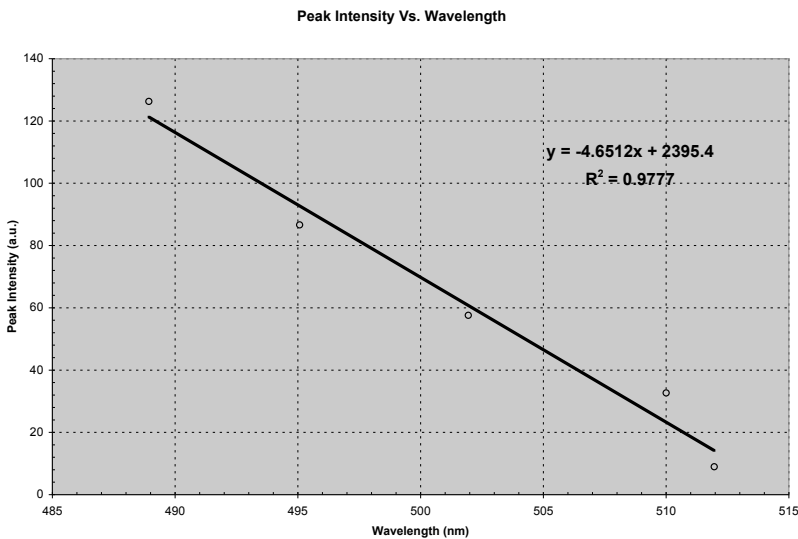


Table 2: Wavelength/Emission Data for Samples from 485 to 520 nm

Wavelength (nm)	Emission Standing Sample	Emission Stirred Sample
485	63.19	24.57
490	63.86	25.53
495	62.20	25.02
500	60.33	24.83
510	53.21	22.66
515	50.84	22.16
520	46.57	20.21

Table 3: Results of measured Sr concentration in water with sediment after 5 days

Wavelength (nm)	Calculated ppm Sr standing	Calculated ppm Sr stirred	Original Amount Added ppm Sr
485	31.4	18.2	50.0
490	31.2	18.1	50.0
495	30.4	17.5	50.0
500	30.1	17.3	50.0
510	28.3	16.2	50.0
515	28.6	16.1	50.0
520	27.7	15.6	50.0
Average ppm	29.7	17.0	
± stand dev.	1.5	1.0	
Ratio stirred to standing:		57.3% ± 0.7%	
Ratio to original			
standing		59.4% ± 2.9%	
stirred		34.0% ± 2.1%	

Bibliography:

1. C.E. White and R.J. Argauer, Fluorescence Analysis-A Practical Approach, Marcel Dekker, New York 1970
2. J.D. Winefordner, editor, Trace Analysis: Spectroscopic Methods for Elements, in Chemical Analysis, Volume 46, John Wiley & Sons, New York, 1976, p 263-271.
3. Jiri' Stary'. The Solvent Extraction of Metal Chelates, Pergamon Press, London, 1964.
4. R.E. Jackson and K.J. Inch, J. Contaminant Hydrology, **1989**, 4, 27-50.
5. K.E. Bencala, et al., Water Resources Research, **1983**, 19(3), 725-731.