CHEM 506 – Final Exam

The Analysis of a Murder.

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a) The Case Study

Even to a homicide detective in a major city, this was shocking. London Police Inspector Derek Peters looked down at the headless, limbless torso of a dark-skinned seven-year old boy lying on a slab in the London morgue. Overcoming his revulsion, he asked Dr. Wooley, the Coroner, to fill him in on the circumstances under which the body, that had been termed simply "Adam", had been found.

Dr. Wooley said, "The victim's nude torso was found floating in the Thames earlier this morning. A boatman saw it, dragged it from the river, and called us. The dismemberment of the body together with the fact that a number of candles were found floating near the body make me think that the boy was killed in some sort of a ritual ceremony."

Derek recognized that he had a tremendously difficult job ahead of him. Identifying the boy would be a major challenge; Adam's murderer or murderers had obviously intended to make that task nearly impossible. But Derek was determined to identify the boy, and to bring those responsible for his murder to justice.

Returning to Scotland Yard, Derek sought out the brilliant forensic scientist that he had worked with so many times in the past, Dr. Marie O'Sullivan. Dr. O'Sullivan's background was in analytical chemistry and biochemistry, and she was an extremely clever and dogged investigator. Derek was confident that she could help him in his quest for Adam's killer.

As he entered her office later that day Marie said, "Hello Derek, I've been expecting you. I heard about the body found in the Thames, and when I learned that you were assigned to the case I thought that I'd be seeing you soon."

"As usual, you're way ahead of me Marie, but that's no surprise. Do you have any thoughts on how we can identify the victim?"

"I do. I will visit Dr. Wooley and obtain samples that we can use to study the trace chemical content of his bones. I will also ask that the people at the morgue study the victim's stomach contents."

Later that same day, at Marie's request, technicians at the morgue studied the contents of the young victim's stomach. The nature of its contents indicated that the boy had been in the United Kingdom for less than two days before his death. Trace pollens present in his stomach were found to be of foreign origin.

Upon learning of these results, Marie said, “A good friend of mine, Professor Kenneth Pyle of the University of London, does research on the global distribution of strontium in soils. If we are lucky, he may be able to correlate the strontium concentration in the victim’s bones with the region in which he grew up. The boy’s stomach contents may give us some idea how long he has been in the United Kingdom. ”

“How could the strontium content of his bones tell us where he may be from? Wouldn’t a study of his DNA be more useful?”

“The composition of the boy’s DNA would certainly be very useful in determining his familial origin, but wouldn’t necessarily be helpful in locating his home. However, the elements present in the soil of a region accumulate in the foods grown there and, in turn, they accumulate in the bones of the people who consume the food. We may be able to use Professor Pyle’s database to get some insight into the region in which the boy spent most of his life.”

Marie telephoned Professor Pyle that day and set up an appointment to visit him the next afternoon. In the meantime, Derek contacted Dr. Wooley to request the bone samples that the investigators believed would aid them in their quest to identify Adam.

Derek and Marie arrived at Professor Pyle’s comfortable but cluttered University office the following afternoon. Professor Pyle was already familiar with the basics of the Adam case from the media accounts that he had seen. Marie and Derek quickly filled him in on some details of the case that had not been provided to the media and asked for his assistance in the ongoing investigation. They carefully omitted mentioning the lab's findings about Adam's possible African origins so that they did not bias Professor Pyle's studies.

"Of course I'd be willing to help," said Professor Pyle. "It isn't often that someone who investigates the variations in the strontium concentration of soils as his vocation and his hobby has a chance to help out in anything as worthwhile and intriguing as this."

Derek asked, "Can you give us an idea of what the information that you hope to obtain can do for us Professor Pyle?"

"From what you have told me, the most likely regions of origin for the victim are either the islands of the Caribbean or the continent of Africa. The variation in strontium concentration between those locations is such that I should be able to immediately determine which, if either, of those sites is the correct one. If we are lucky, we may be able to narrow Adam's likely area of origin even further."

Marie said, "That is what we were hoping for, Professor Pyle. The Coroner's office will deliver the bone samples from Adam's body to your laboratory later today. I needn't tell you that time is critically important in this case. The press is in a great uproar over it, and we are feeling a good deal of pressure to move quickly on its solution. Can you give us any idea when we might have your judgment on Adam's region of origin?"

“I shall begin my analysis of the bones as soon as they arrive. If all goes well, I should have some preliminary information for you by this time tomorrow afternoon.”

The following afternoon, Professor Pyle called Derek and Marie to tell them that the strontium content of Adam’s bones was extraordinarily high and indicated that Adam had spent almost all of his short life in sub-Saharan Africa.

“That’s wonderful, Professor. Can you give us a closer estimate of where Adam may be from?”

“We were lucky, the concentration of strontium in Adam’s bones is quite high. It indicates that he may be from Nigeria. Regions of that country have areas of very high strontium content in their soils, but my database for Nigeria is not sufficiently detailed to allow me to give you any more information than that just now.”

By this time Marie and Derek’s boss, Chief Inspector Warner, was under heavy pressure from his own superiors as well as from the media to come up with leads in the “Adam Case”, as it had come to be known.   When they visited the Chief Inspector to inform him of the progress they had made in the case, he was delighted. He quickly recognized what a valuable resource Professor Pyle was and asked if the Professor could provide any more detail.

“Professor Pyle has told us that if he had a collection of bone samples from throughout the areas of Nigeria that he suspects Adam may be from, we might be able to narrow the search area considerably.”

“Can we get the samples that he needs?”

“Derek has volunteered to travel to Nigeria and collect the samples that Professor Pyle needs if you are willing to have him go there, Chief Inspector,” said Marie. “I would like to be assigned to coordinate the sample handling and communication between Derek and Professor Pyle.”

“ Done. As you know, there is a lot of pressure on us to get results in this case, so move as quickly as you can. Just let me know what resources you need and I shall do my best to see that you get them.”

Two days later, Derek landed in Nigeria and headed for the areas that Professor Pyle thought might yield important information. Following Pyle’s instructions, he collected soil samples from locations the Professor had specified, gathered animal bones from local markets, and visited the pathology departments of universities where he obtained samples of human bones from throughout each region. As he collected each sample, he recorded its precise origin, carefully packaged it and promptly shipped it by air to Marie in London. She conveyed each sample to Professor Pyle, passed on Derek’s description of its nature, and pinpointed its origin. As the samples were analyzed for their strontium content, the Professor's database of strontium distribution in Nigeria grew increasingly detailed.

As Professor Pyle and Marie compiled the data, they began to assemble a more detailed map of the variations in strontium concentration in the selected regions than had previously been possible. The team of investigators used these data to greatly narrow the area in which Adam was thought to have lived, and to formulate a strategy by which the person(s) responsible for his murder could be apprehended.

Your Turn

The fictional characters in this case study have done their work. It is now up to you to put together the final pieces in the mystery that surrounds Adam's death, and to solve the crime. Inductively coupled plasma (ICP) emission spectrometry was used to determine the strontium concentration in each of the bone samples given. Use the data sets that you are given to locate Adam's region of origin. Having accomplished these tasks, you are to: 1) decide what significance the nature of the pollens found in Adam's stomach could have to this investigation; 2) devise a plan that could lead to the identification of the person or persons who took Adam from his home in Nigeria to his death in London based on your analytical data; 3) write a report to Chief Inspector Warner of Scotland Yard detailing the nature and outcome of your work.

b) The Experimental Procedures

I. Determination of strontium to calcium ratios in bone samples:

Dried sample (~0.1 g, accurately weighed) was dissolved in about 2 mL of nitric acid at room temperature with stirring. The transparent solution was volumetrically diluted to 50 mL. The solution was analyzed directly on the ICP spectrometer. Calcium and strontium were monitored at 370.603 nm and 421.552 nm, respectively. These wavelengths were chosen because they are relatively free of spectral interference. Also, their dramatically different sensitivities allowed the simultaneous quantification of both calcium and strontium in the solution, despite their large concentration differences. Sample loss may occur during digestion and dilution, yielding low values. Low values could also result from incomplete ashing of the bone, or absorbed water contributing to the sample weight. These actual or apparent losses may be eliminated by comparing the $[Sr^{2+}]/[Ca^{2+}]$ ratio in each sample, as the $[Ca^{2+}]$ would scale proportionally with the $[Sr^{2+}]$.

I. ICP Determination of strontium to calcium ratios:

External standards were prepared and analyzed to generate calibration curves for the determination of both calcium and strontium, as well as to determine the quantitative limit of the method. The ICP-AES spectrometer used in this procedure is capable of detecting traces of strontium in the parts per trillion range. Because of this high sensitivity, great care must be taken to avoid sample contamination from environmental sources, such as dust or pollen particles, that could lead to erroneously high results. Therefore, all glassware used in the procedure must be cleaned using a four-hour acid wash followed by a thorough second wash using distilled, deionized water to remove traces of strontium contamination. The use of careful analytical technique allows for accurate quantitation in the needed 3 ppm (w/v) range.

II. Required Chemicals:

Calcium hydroxyapatite (1306-06-5)

Calcium chloride, anhydrous (10043-52-4)

Dibasic sodium phosphate (7558-80-7)

Monobasic sodium phosphate (7558-79-4)

Nitric acid (7697-37-2)

Strontium nitrate (1004-2-76-9)

Strontium chloride (10476-85-4)

Strontium chloride hexahydrate (10476-52-4)

III. Required Equipment

Analytical balance

Bunsen burner

Ceramic crucibles

Digital micropipette

Drying oven

Inductively coupled plasma-atomic emission spectrometer

Stirring apparatus

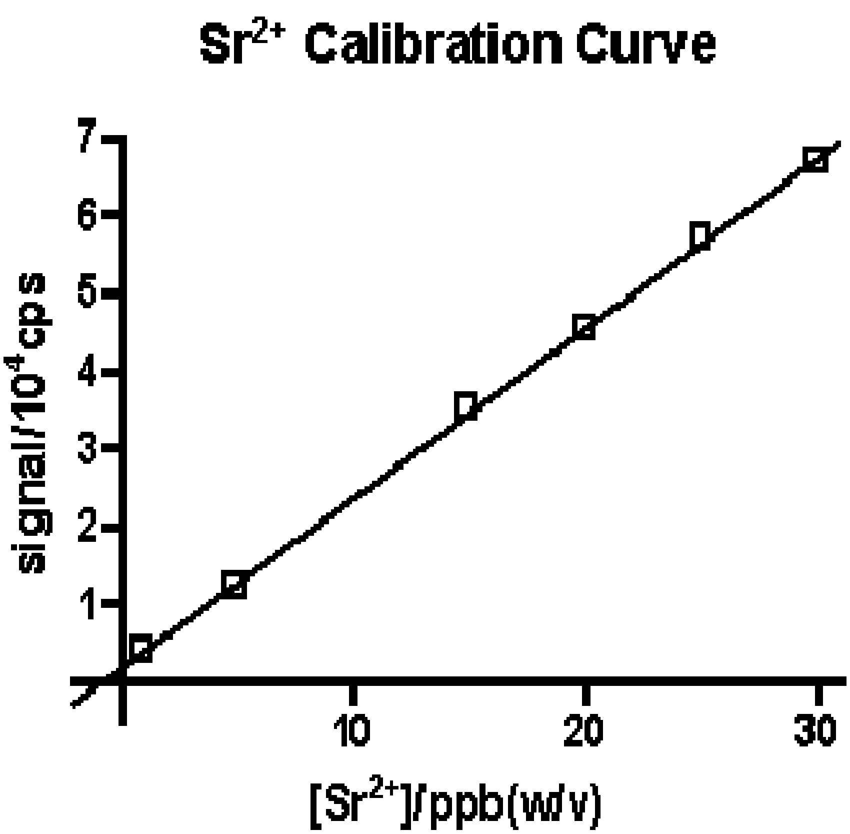
IV. Safety and Disposal

Safety glasses and protective gloves must be worn at all times. Any strontium containing materials must be collected in a properly labeled waste container. Nitric acid is a strong acid and a powerful oxidizing agent. If it should come in contact with skin, it should immediately be flushed extensively with water.

VI Results:

Calibration and Determination of the Quantitation Limit and other Figures of Merit

A 100 ppm Sr^{2+} solution was prepared by dissolving 0.3042g of strontium chloride in water to a total volume of 1L. Aliquots of this solution were used to prepare 50 ppm, 40 ppm, 30ppm, 25 ppm, 20 ppm, 15 ppm, and 5 ppm solutions. The ICP-AES signals from these solutions were used to generate the calibration data below.



The standard calibration curve is fit with a straight line with a slope of 0.2182 ± 0.002239 (s.d.) and a y-intercept of 0.1840 ± 0.04264 (s.d.), with $r^2 = 0.9996$. The detection limit for the method is therefore _________, and the quantitation limit is 2.0 ppb. The calculated background concentration is 0.84 ppb, which is detectable but below accurate quantitation. The fluctuations in the signal for a background sample indicate a quantitation limit for the instrumental method of 60 pptr. The deviations of the data from the straight line are much higher than the instrument detection limit, but also highly reproducible, implicating determinate errors in the preparation of the standards.

Bone Analysis:

Sample	Sample Size (g)	ug Sr in Sample	[Sr] in Sample (ppm)	Avg. [Sr]	Precision
A	0.5044	15.77			
	0.5488	16.86			
	0.6117	18.17			
	0.8646	26.00			
B	0.8785	26.41			
	0.6838	20.34			
	0.7124	21.40			
	0.9101	28.00			
C	0.7968	25.22			
	0.6521	18.23			
	0.8967	29.14			
	0.5366	15.84			
D	0.5993	17.33			
	0.9928	28.03			
	0.6793	19.16			
	0.5954	17.24			
E	0.5529	17.31			
	0.5971	20.53			
	0.7352	24.34			
	0.9417	31.01			

Sample A: Adam's bone tissue.

Sample B: Bone tissue from Benin City region.

Sample C: Bone tissue from Ibadan region.

Sample D: Bone tissue from Argungu region.

Sample E: bone tissue from Yola region.

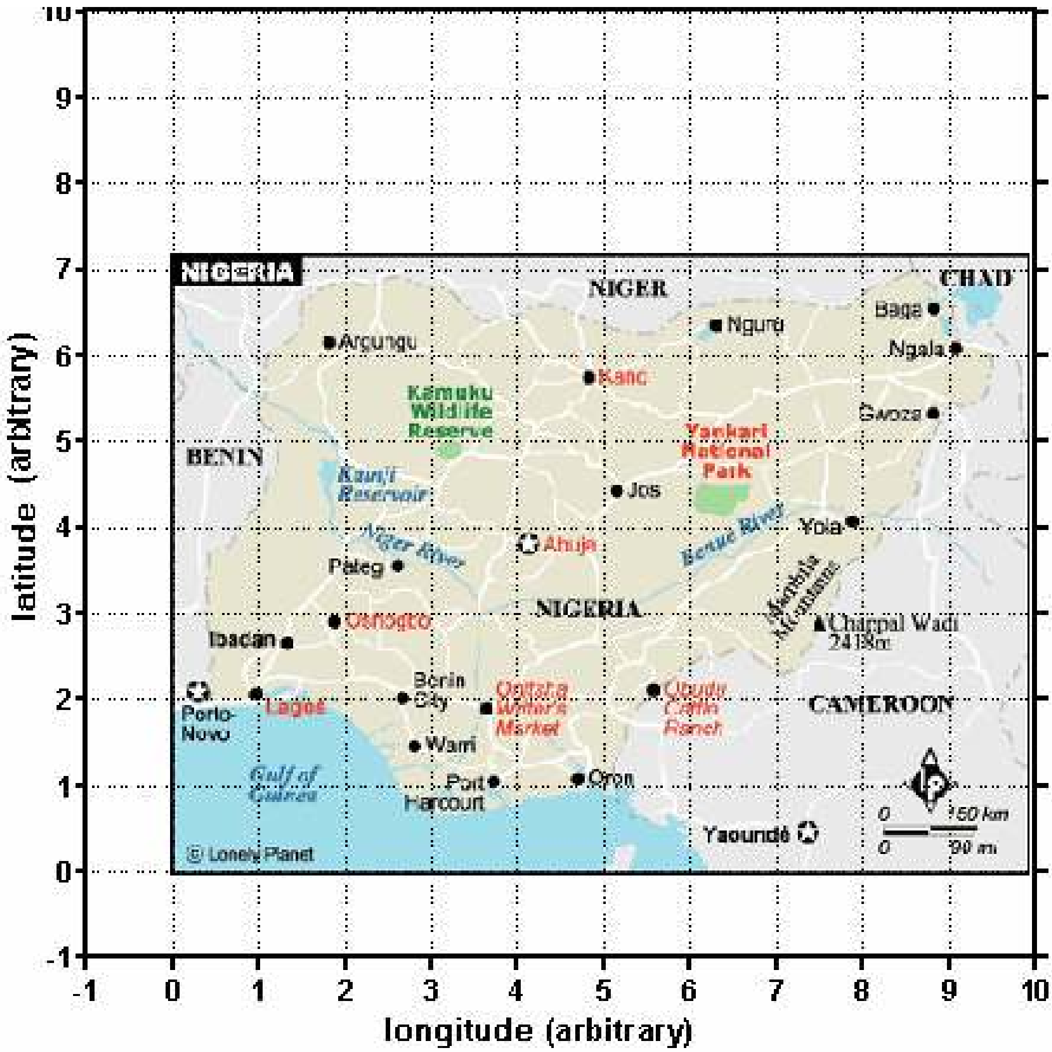
Discussion questions to include with report:

1. Complete the map of the African nation of Nigeria that clearly marks the cities of interest and print a copy of the map.

2A. While preparing 100.00 mL standards for a trace analysis of strontium (AW = 87.62 g/mol), a careless student spills a small amount of strontium chloride hexahydrate (FW = 266.617 g/mol) creating an airborne dust. What is the minimum edge length of a perfectly cubic airborne crystal of strontium chloride hexahydrate (density = 1.96 g/cm^3) that can alter the concentration of the standards by 1 ppb (w/v)?

2B. Is this crystal from 1A visible to a casual observer in a lab setting? How could the crystal cause contamination? How could you prevent contamination with this type of source? *For perspective's sake, a human hair is about 70 μm thick.*

3. Describe why two stages of sampling may be necessary to pinpoint Adam's origins.



Example location data:

X-axis ("longitude")	Y-axis ("latitude")	measured value	location
1.8	6.1		Argungu
			Benin City
			Oron
			Ibadan