C9 Age-Dating Leaded Gasoline Releases

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The goals of this presentation are to learn how to use the ALAS model in order to age-date leaded gasoline releases to the underground environment and how to evaluate the results for an environmental forensic litigation case.

Introduction

Richard W. Hurst introduced the ALAS (anthropogenic lead archaeostratigraphy) model at the 1996 National meeting of the American Society of Mass Spectrometry in Portland, Oregon. This model uses the changes in lead isotope ratios over time (in years) to predict the age of a gasoline from the organolead antiknock additives such as tetraethyl lead (TEL). The ALAS model used calibration samples from the literature as well as from gasoline collections. However, the major assumption is that these calibration points represented lead in gasolines nation-wide and were consistent over a one-year time period. This seems to be a "stretch" for either common sense or scientific data.

In a recent paper by Hurst[1], the ALAS model calibration has been verified by an independent method. Using the lead mining records and literature estimates of lead recycling, Dr. Hurst calculated the lead isotope ratios over time from these data. The correlation between the ALAS model obtained from samples and the ALAS model from lead used in the U.S. is excellent. (The correlation coefficient [R] for the time frame of 1950 to 1990 is 0.967.) This strongly supports the ALAS model's usefulness in age-dating leaded gasolines anywhere in the U.S. It also extends the ALAS model to the 1920s when TEL was introduced into gasoline.

How to Use the ALAS Model

Soils contaminated with a petroleum product(s) or a free phase petroleum product(s) from a soil boring or monitoring well is taken as a sample. A soil sample should contain a significant quantity of the petroleum product.

Step 1) Gas Chromatography with a Flame Ionization Detector (GC/FID)
The initial test is to determine what the petroleum product or products are. The easiest analytical method is to use GC/FID

to "fingerprint" the petroleum sample. A solvent extraction is needed to prepare the soil sample for analysis. The free liquid product must be diluted with a solvent prior to analysis. If the product is at least in part gasoline, then the analysis is continued to Step 2.

Step 2) Gas Chromatography with an Electron Capture Detector (GC/ECD)
The solutions used in the GC/FID experiment can be used in the GC/ECD analysis if the solvent is relatively inactive for the electron capture detector. Step 2 is used to determine the presence or absence of the various organolead gasoline additives such a TEL. If the organolead additives are present, then the analysis is continued to Step 3.

Step 3) Determination of the Amount of Organolead in the Sample There are two methods for determining the amount of organolead in the sample. The extract can be digested with nitric acid and total lead determined by Inductively Coupled Plasma (ICP) or Atomic Absorption Spectroscopy (AAS). The specific organolead compound or compounds can be determined using GC/ECD, if the standards are available, by quantitative GC methodology.

Step 4) Lead Isotope Ratio Determination
The sample is sent to a laboratory with a multicollector mass spectrometer for the measurement of the abundance of lead isotopes 204, 206, 207, and 208. These measurements are very accurate and precise. The data is calculated using a "delta" notation based on equation 1.

$$*^{206}\text{Pb ALAS} = 1000 \times \frac{[\text{Pb}^{206}/\text{Pb}^{207}\text{ sample} - \text{Pb}^{206}/\text{Pb}^{207}\text{ standard}]}{\text{Pb}^{206}/\text{Pb}^{207}\text{ sample}}$$

The delta value from the mass spectrometric analysis of the lead isotope is used with the ALAS model to obtain the date of the organolead additive in the gasoline found in the soil or as a free liquid in the environment (Figure 1).

 ** Presenting Author*

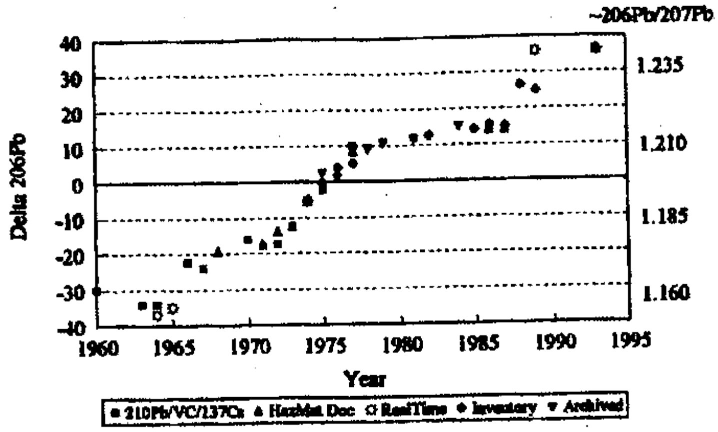

FIGURE 1: (FT)ALAS model calibration curve. (COP Richard W. Hurst, 1997; Hurst. 2000.)

What Does the Result Mean?

The interpretation of the ALAS model result is not trivial due to a number of factors.

1) Most corner gas stations that sold leaded gasolines did not sell premium leaded gasoline after 1981, sold leaded gasoline in 1985 that contained a lower concentration of lead than the immediate preceding years, and did not sell leaded gasoline after January 1986.[2]
2) The slope of the ALAS model of $*Pb^{206}$ versus time in years is such that age-dating is accurate to ± 1 to 2 years. Before 1965 and after 1985, the age-dating has a large error term due to the horizontal nature of the calibration curve.
3) The type of gasoline release at the site is also important. If there is a single catastrophic release, then the age-dating value is very good. But most underground storage tank leaks are not catastrophic. These leaks are not consistent or constant. They depend on where the hole in the tank is located and how rapidly the hole corrodes to a larger opening. Piping leaks could be similar to tank leaks.

In these circumstances, the ALAS model result is a weighted average of the lead from years of a slow, leaded gasoline release. Thus, the ALAS model's error term is not the range of time for the release. This time range needs to consider the site history such as tank abandonment, documented releases, and the timing of leaded gasoline sales at the station to aid in rendering a time frame for the leaded gasoline release.

All of these interpretations are based on the knowledge that gasoline production, transportation, storage, distribution, and use is a short period of time compared to the year in the ALAS model.

Errors

Even with this careful, stepwise procedure one can obtain an erroneous result. Caution is especially important in a soil sample where native lead in the soil can be more abundant in the extract for the lead isotope measurement than the lead from the gasoline. In this case, an ethyl alcohol extract of the organolead from the soil will be better than the usual dilute nitric acid digestion.

Other Uses

Used motor oil contains wear metals and one of the most prominent wear metals is lead. Used motor oil from gasoline engines will contain a low percentage of gasoline and that gasoline may have been leaded. The same stepwise procedure is used for the used motor oil for age-dating purposes. Now the ALAS model result depends on the average age of the engine bearings as the source of lead wear metal. One needs to assume that the lead used for these engine bearings has the same history as the lead used to produce the organolead gasoline additives.

Cases

The presentation will use case studies to illustrate the ALAS model in environmental forensic applications.

Conclusion

The environmental forensic use of the ALAS model for age-dating leaded gas releases to the environment is scientifically defensible. The analytical chemistry needs to be done in a stepwise manner and caution is necessary to avoid background natural lead in soil from compromising the result.

1. Hurst, Richard W., "Lead Isotopes as Age-sensitive Genetic Markers in Hydrocarbons. 3. Leaded Gasoline, 1923-1990 (ALAS Model)," Environmental Geosciences, Vol. 9, No. 2, pp.43-50, 2002.
p. 40CFR, Parts 61 to 80, Subpart B-Controls and Prohibitions, 80.20, 1201, Rivised as of July 1, 1994.

Gasoline, Lead, Age-Dating