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# Extraction methods for iodine from crude oil systems for the determination of $^{129}\text{I}/^{127}\text{I}$ ratios

Sharon Tullai

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EXTRACTION METHODS FOR IODINE FROM CRUDE OIL SYSTEMS  
FOR THE DETERMINATION OF  $^{129}\text{I}/^{127}\text{I}$  RATIOS

SHARON TULLAI

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THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

Dr. Laura Tubbs  
Project Adviser

Gerald A. Takacs  
Department Head

Illegible Signature  
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Rochester Institute of Technology  
Rochester, New York 14623  
Department of Chemistry

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ABSTRACT

$^{129}\text{I}/^{127}\text{I}$  ratios were investigated as a potential for dating and tracing studies of crude oil systems.  $^{129}\text{I}/^{127}\text{I}$  ratios were measured using a tandem accelerator mass spectrometer located at the University of Rochester. Carrier-free methods for AgI preparation are discussed for formation waters, petroleum, and source and reservoir rocks. Formation water extractions include the use of oxidizing and reducing agents to extract iodine into carbon tetrachloride. Samples prepared in this way gave good ratio measurements with no contamination. Two methods for iodine extraction from petroleum are employed. The first is a sodium biphenyl extraction which will extract up to 90% of iodine but has serious limitations due to contamination of the solvent. The second method for petroleum is a combustion method which can recover at least 50% iodine with minimal contamination if the proper precautions are observed. Only 10% of iodine can be recovered in the rock samples at this time using a nitric acid digestion in a closed system and collecting iodine in carbon tetrachloride from the vapors.

## I. INTRODUCTION

The theory of using radioactive isotopes as a method of dating was first initiated by W.F. Libby in 1934 when he successfully measured the radioactivity of  $^{14}\text{C}$ . [1] In 1949, Arnold and Libby demonstrated the feasibility of carbon-14 dating by analyzing a suite of archaeological samples of known age. Two years later it was found that the  $^{14}\text{C}/\text{C}$  ratios in the biosphere remain relatively constant within narrow limits and are apparently independent of latitude. Carbon-14 dating can now be used fairly routinely with good precision on most organic materials. [2]

This method has some serious limitations which eliminate its use in many situations. One limitation is that only carbon containing materials can be used for this method, second, the material must be able to exchange  $^{14}\text{C}$  with the atmosphere, and the third limitation is that the half life of  $^{14}\text{C}$  is too short to investigate situations older than 40,000 a.\* Since the advent of carbon-14 dating until the present, researchers have investigated other isotope systems for dating purposes. Today, in geology, many different dating systems are used; K-Ar, Rb-Sr and Re-Os, are just a few examples. [2] Although there are many dating schemes, there are still materials for which these isotopes cannot be used, one of which is crude oil.

The use of radioisotopes is not restricted to dating. In hydrology, geology, and oceanic and atmospheric sciences, isotopes such as  $^{36}\text{Cl}$ ,  $^{10}\text{Be}$ , and  $^{129}\text{I}$  are used as tracers. [3-9]  $^{36}\text{Cl}$  and  $^{129}\text{I}$

\* a = years, Ma = million years.

have been used to trace ground water and ground water contamination in the Yucca mountains, Southern Maryland, and Sweden[4,5], to investigate hydrothermal systems and mineral deposits in the Cherry Hill region of California[6], and to investigate radioactive waste repositories by studying uranium deposits.[7]  $^{36}\text{Cl}$  and  $^{10}\text{Be}$  have been used in Greenland ice cores to study the history of sun spot activity and to make comparison of arctic and antarctic records from polar ice.[8,9].

In this work, the  $^{129}\text{I}$  system was investigated for potential application to dating or tracing studies of crude oil systems. This thesis focuses on the development of chemical methods used for sample preparation and isotope measurement. Although using  $^{129}\text{I}$  dating for this system is still at an exploratory and speculative stage, it has the potential for dating old brines and hydrocarbons, or more specifically, crude oil systems.  $^{129}\text{I}$  has a half-life of 15.9 Ma and there is only one stable isotope of iodine,  $^{127}\text{I}$ . There are two major forms of natural production of  $^{129}\text{I}$ , in the atmosphere by the interaction of cosmic rays on  $^{129}\text{Xe}$  and in the earth's crust as a product of spontaneous fission of  $^{238}\text{U}$ . A third source of  $^{129}\text{I}$  input is the fallout of nuclear bomb tests and nuclear power stations which is referred to as the anthropogenic input of  $^{129}\text{I}$ . This anthropogenic input is responsible for increasing the atmospheric ratio by more than two orders of magnitude.[10,11]

Once  $^{129}\text{I}$  enters the marine system it follows the same geochemical pathway as  $^{127}\text{I}$ . Iodine is considered a geochemically, very mobile element, having a residence time in the oceans of about 300,000 a. This leads to the assumption that iodine is isotopically well mixed in the oceans. This assumption, the fact that iodine is closely associated with

organic material, and the relatively long half life of  $^{129}\text{I}$  suggest that this system can be used for age determination of buried organic material namely petroleum.[10,11]

The oil formation process starts with organisms in the ocean which die and eventually fall to the ocean floor. The organic material begins to mix with the ocean sediments and through millions of years of burial and diagenesis (physical and chemical changes in sediment after deposition that converts it to consolidated rock), a fraction of the material slowly transforms to fluid and gaseous hydrocarbons. In the process, these sediments are compressed into permeable rock, called the source rock where the hydrocarbons will mature. Once the oil has matured it will migrate laterally up an inclined layer of permeable rock until it reaches a sealing layer where it might accumulate in a trap and form an oil reservoir. In general, petroleum is usually mined in the reservoir rock but it can be mined from the source rock with greater difficulty.[12]

During the maturation process, the fate of the iodine is unknown. A comparison between typical marine organic material (50 ppm I) and crude oil (<3 ppm I) is evidence of a net loss of iodine occurring during maturation.[11] The question that needs to be addressed is whether the iodine is lost from the organic material or an exchange and loss of iodine takes place concurrently. In the former case, the  $^{129}\text{I}$  could directly be used for the determination of the burial age of the organic parent of the petroleum. If an exchange is taking place, the ratios will be a little more complicated to interpret: the  $^{129}\text{I}$  concentrations would reflect the isotopic composition of the source rock which might have, depending on the uranium content of the rock, a significant amount of in-situ production of  $^{129}\text{I}$ . If the uranium content in the source rock and reservoir rock is different (typically, source rocks will have higher

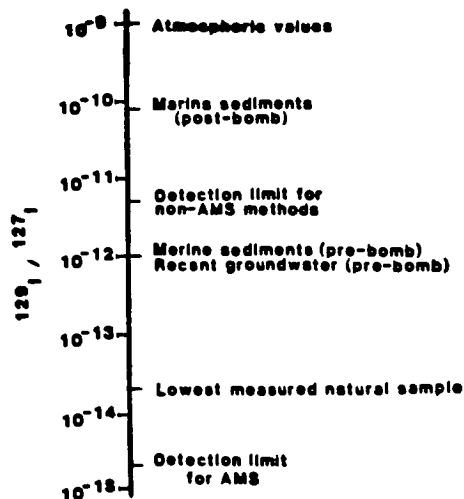


concentrations of uranium than reservoir rocks because of the common association of uranium with organic material) and if the exchange of iodine is limited to the period of maturation (the time spent in the source rock), the iodine composition in petroleum will be related to the time of expulsion from the source rock.[10]

Samples can be taken from each step of the oil formation process where the iodine can exchange or be bound up by various materials. These samples include ocean sediments, source rock, reservoir rock, petroleum and any waters associated with the petroleum.  $^{129}\text{I}/^{127}\text{I}$  ratios can then be measured in these samples to aid in the interpretation of the net loss of the iodine. Ratio measurements of ocean sediments have determined the pre-bomb ratio to be  $2 \times 10^{-12}$  (Figure 1). The next measurements needed are the  $^{129}\text{I}/^{127}\text{I}$  ratios in the source rock, reservoir rock, petroleum, and formation waters.

Because of the very low concentrations of  $^{129}\text{I}$  in nature (isotope ratios of  $^{129}\text{I}/^{127}\text{I}$  are typically around  $10^{-12}$ ), this system is below the detection limit of counting and conventional mass spectrometric methods. With the development of tandem accelerator mass spectroscopy (TAMS), the detection limit has been lowered to  $2 \times 10^{-15}$  (see Figure 1) which will accommodate the natural  $^{129}\text{I}$  concentrations, and allow a dating capability of about 80 Ma.[11]

Figure 1: Detection limits and typical values for  $^{129}\text{I}/^{127}\text{I}$  ratios.[11]



## II. CHEMICAL PROCEDURES

The samples for ratio measurements using tandem accelerator mass spectroscopy (TAMS), are in the form of AgI and at least 1 mg of iodine is needed to sustain a useable current in the accelerator. Isotopic ratios are independent of concentration and therefore high chemical yields are not imperative for this project. High yields however, are to our advantage for sample preparation time, cost and convenience.

Iodine in macro quantities is a very useful element for oxidation and reduction purposes. The oxidation-reduction potentials of iodine can, in some samples, be used to our advantage, but in other samples, such as rocks, with low iodine content, these reactions are inhibited or masked by other more prevalent reactions that are occurring. Detection is possible through iodide electrodes, gravimetrically, titrimetrically and potentiometrically with  $\text{AgNO}_3$ . Our samples typically fall around the lower limits of detection in the methods mentioned or have interferences which give unstable measurements at the lower limits, therefore we must resort to other methods of detection which are sometimes more tedious and time consuming. The methods include a spectrophotometric method which involves iodine in  $\text{CCl}_4$  and an indirect method involving the oxidation-reduction reaction between ceric and arsenic ions.

### A. TOTAL IODINE CONTENT

#### 1. Iodine in Carbon Tetrachloride Method

Iodine forms a brilliantly colored complex with carbon tetrachloride which can be spectrophotometrically detected at 515 nm. The range of this method is from 1.0 to 100 ppm: the upper limit has not been established because

our interest lies in the lower range. The iodine-carbon tetrachloride complex follows Beer's law in this range, where  $A=ebc$ . A is the absorbance, b is the path length, c is concentration, and e is the extinction coefficient. There is an ASTM method (D-3869) which uses the absorbance of iodine in carbon tetrachloride as part of a method of total iodine in brackish water, seawater and brines where concentrations range from 0.2 - 2000 ppm.[13] Their extraction of iodine from the water, however, is different. In the ASTM method iodine is extracted with the use of HCl and  $\text{NaNO}_3$ , and in this method, iodine is extracted by the method presented in section II.B.1.

#### Apparatus

Bausch and Lomb Spectronic 100.

Volumetric flasks.

#### Reagents

Carbon tetrachloride, reagent grade.

Iodine, reagent grade.

#### Procedure

Prepare standards in the range 0-100 ppm iodine by serial dilution of elemental iodine dissolved in carbon tetrachloride. Measure the absorbance at 515 nm and plot directly, concentration vs. absorbance. Sample absorbances are measured at 515 nm and concentrations are determined from the calibration curve.

#### Discussion

This method works extremely well for samples where iodine can be extracted into carbon tetrachloride. At present these samples include the formation waters, petroleum after the use of the combustion method, and the rocks. A typical calibration curve is shown in Figure 2. The

principal errors inherent in this method is not in the absorbance measurements, but is in the extraction procedure. Since total extraction can not be proven, the concentrations associated with this method are the amounts extracted or the extractable iodine. In those cases where total iodine concentration is known, for example the petroleum samples from neutron activation results, the concentration using this method can be used to calculate yield. The overall error for this method was found through statistical analysis to be three percent.

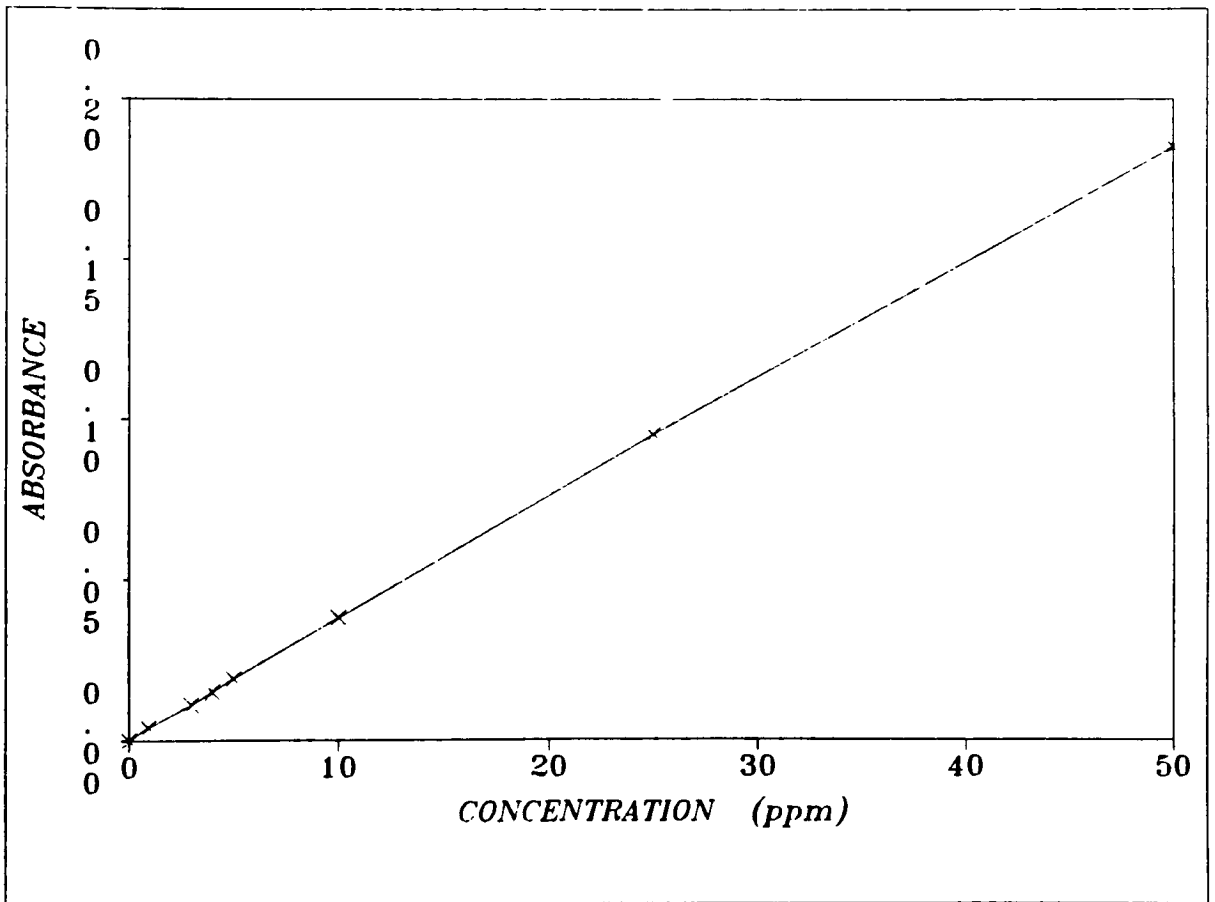


Figure 2: Calibration curve for  $I_2/CCl_4$

## 2. Cerium-Arsenic Redox Method

The procedure outlined below is a redox reaction between cerium (IV) and arsenic (III) ions, where iodine is a catalyst. The net reaction is:



In the range of 0.03-0.2 ppm I the reaction is pseudo first order with respect to iodine.[14-18] This reaction has been well studied for the use in routine work of iodides and iodates in sea water [14] common salt [15] and protein bound iodine.[16,17] Rate kinetics and reaction mechanisms have also been studied in depth.[18]

### Apparatus

Bausch & Lomb Spectronic 100.

Centrifuge tubes, 50 ml disposable .

### Reagents

Arsenous Acid. Dissolve 9.9 g of  $\text{AsO}_3$  in 100 ml of warm 18 M  $\Omega$   $\text{H}_2\text{O}$  containing 4.0 g NaOH. Dilute to approximately 400 ml and acidify with 47 ml of 18 N  $\text{H}_2\text{SO}_4$ . Allow the solution to cool and dilute to 500 ml.

Sulfatoceric acid. Add 20.7 ml of 37 N  $\text{H}_2\text{SO}_4$  to 100 ml of 18 M  $\Omega$   $\text{H}_2\text{O}$ . Dissolve 5.05 g of ceric ammonium sulphate in acid solution and dilute to 500 ml.

Brucine reagent. Dissolve 1.25 g of brucine in 250 ml of 1 M  $\text{H}_2\text{SO}_4$  and store in a brown bottle.

Sodium chloride solution, 23 wt%. Dissolve 30 g of NaCl in 100 ml of 18 M  $\Omega$   $\text{H}_2\text{O}$ . Add 1 drop of  $\text{AgNO}_3$  solution to precipitate any trace amounts of iodide present, and filter.

Iodide standards. Using potassium iodide, prepare a series of standards in the range of 0-0.2 ppm iodide.[10]

### Stability of reagents

The reagents are stable for a period of one to two weeks; longer usage results in unstable reagents and erratic results.

### Procedure

The procedure is described for the preparation of a calibration curve using  $I^-$  standards. To measure samples, replace the word standard with sample and follow the procedure. For samples containing greater than 0.2 ppm iodine, the sample is diluted to scale and a dilution factor employed.

For each standard, place 10 ml of standard, 10 ml of arsenous acid and 0.5 ml of 23 wt% NaCl in 50 ml centrifuge tubes. Cover, and place the tubes in a water bath at 30°C for 30 min. Remove the tubes and allow the solutions to cool to room temperature.

The next step is a timed reaction between ceric and arsenic ions where iodide is a catalyst. The reaction is quenched using brucine. For each standard test tube, six clean test tubes are needed. Add 0.5 ml of brucine reagent to each tube. To the standard test tubes containing the arsenous acid, add 2.5 ml of sulfatoceric solution in 10 second intervals. At intervals of 1,2,3,5,7,8 minutes from the time the first 2.5 ml of sulfatoceric solution is added, quench the reaction by placing 2.5 ml of standard in the test tube with brucine.

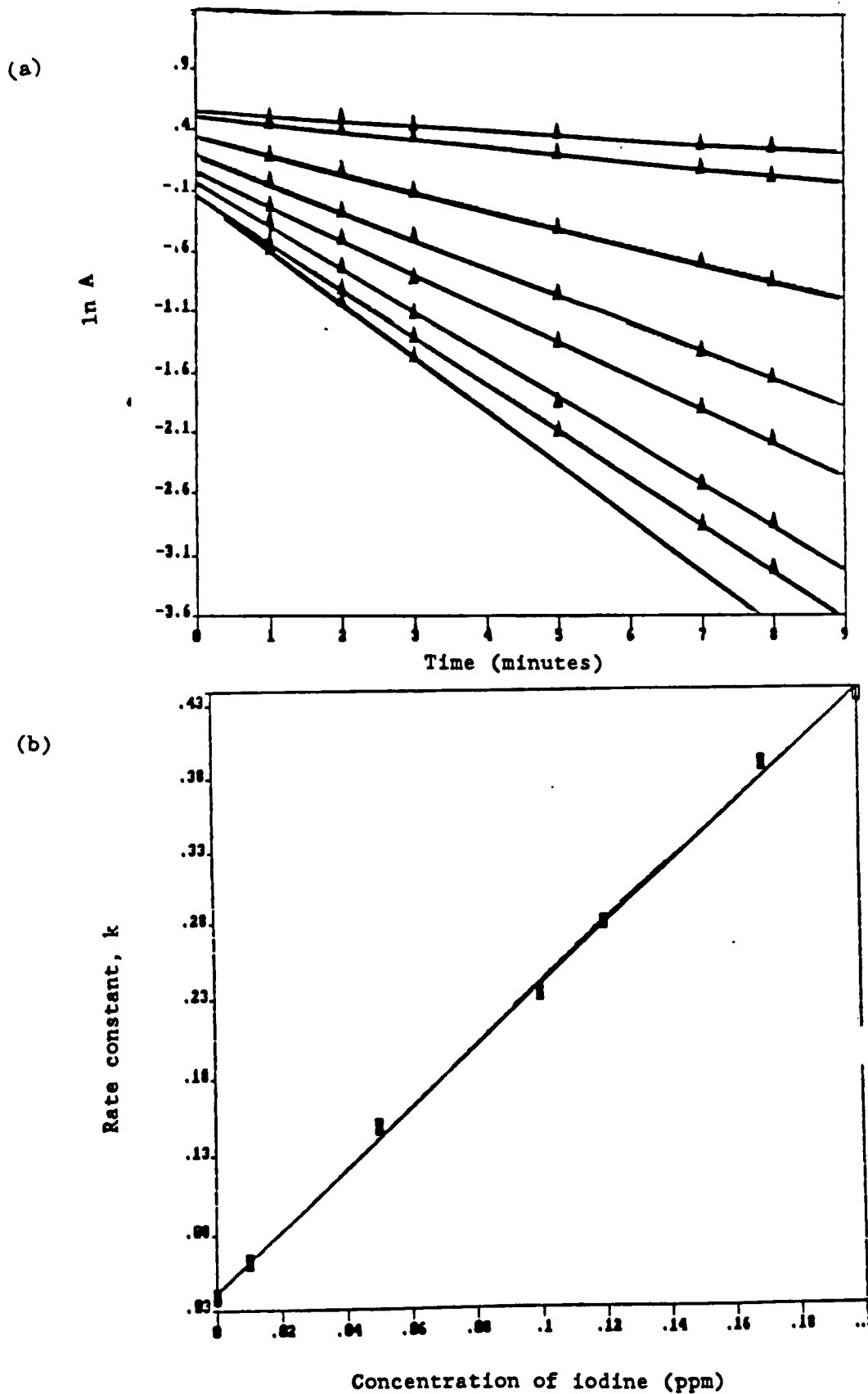
Measure the absorbance of the quenched reactions at 440 nm. The absorbance measured is the cerium ion which is a yellow color. As the reaction continues the yellow color will fade to colorless, indicating the oxidation of the Ce(IV) ion to Ce(III) ion. After all color has faded from the original reaction vessels (usually one hour), read absorbances of the original standard test tubes. This background absorbance is then subtracted from the previous readings.

### Analysis

The reaction between ceric and arsenic ions is a pseudo-first order rate reaction with respect to iodine [18], therefore the slope of the line,  $\ln A$  vs. time (min), is the rate constant,  $k$ . A calibration curve can be obtained by plotting  $k$  vs. concentration. Figure 3 (a)&(b) is an example of a standard calibration curve, where (a) is the plot of  $\ln$  Absorbance vs. time in minutes for each iodine concentration, and (b) is the plot of  $k$  vs. concentration of iodine in ppm. Points which deviate from linearity can be eliminated based on statistical considerations. Sample concentrations can then be read from the calibration curve.

The detection limit for the ceric-arsenic analysis was found to be 0.03 ppm in good agreement with previous results.[18] The values obtained agree well with results from neutron activation analysis. This method is inhibited by oxidizing or reducing agents and therefore its use is restricted to those cases where these agents are not present in the sample. This method then, is used primarily with the method presented in section II.B.2.a.

Figure 3: (a) Plot of  $\ln A$  vs. time (min) for the iodine catalysed ceric-arsenic reaction. The slope of these lines are the rate constants,  $k$ . (b) Calibration curve; the rate constant,  $k$  vs. concentration in ppm.





## B. EXTRACTION PROCEDURES

### 1. Formation Waters

The formation waters are the waters that are present around and associated with the crude oil. It is important to note any similarities in ratios between oils and waters in order to see if there might be any atmospheric contamination which could effect the  $^{129}\text{I}/^{127}\text{I}$  ratio of the oil. These waters are usually high in  $\text{Cl}^-$  (40,000 ppm) and contain about 13-18 ppm extractable iodine, mostly as iodide but partly in higher oxidation states (iodate, periodate). The water, which is usually clear, still needs to be filtered to remove any oily substance on the surface. This does not cause any problems with the extraction procedure.

The extraction method takes advantage of the ease with which iodine is oxidized and reduced. The various states of iodide are not a problem. Since most of the iodine is in the most reduced state,  $\text{I}^-$  is oxidized to  $\text{I}_2$  with hydrogen peroxide in an acidic solution and then the higher oxidation states are reduced to  $\text{I}_2$  with hydroxylamine hydrochloride.

[19] This method also takes advantage of the fact that iodine forms a brilliantly colored complex with carbon tetrachloride. [13] The use of  $\text{CCl}_4$  serves two purposes, first, to separate and concentrate iodine from the water and second to measure the amount of iodine extracted (see section II.A.1).

#### Apparatus

Bausch and Lomb Spectronic 100.

Separatory funnels, cleaned with a  $\text{HNO}_3$  wash,  $\text{NH}_4\text{OH}$  wash and rinsed with 18 M  $\text{H}_2\text{O}$ .

Centrifuge tubes, 50 ml.

### Reagents

Carbon tetrachloride ( $\text{CCl}_4$ ), reagent grade.

Nitric acid ( $\text{HNO}_3$ ), concentrated.

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), 30%.

Hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ), 1 M.

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), concentrated.

Sodium bisulfite ( $\text{NaHSO}_3$ ), 1 M.

Sodium chloride ( $\text{NaCl}$ ), approximately 4000 ppm.

Silver nitrate ( $\text{NaNO}_3$ ), 0.1 M.

Potassium iodide ( $\text{KI}$ ), Banco brand.

### Procedure

Filter enough water to obtain at least 2-4 mg of iodine. Transfer 100 ml of the filtered water to a clean separatory funnel and acidify with 1-2 ml of  $\text{HNO}_3$ . Add 5 ml  $\text{CCl}_4$  and shake. Make sure to vent any gases which form. Add 1-2 ml  $\text{H}_2\text{O}_2$  and shake again.  $\text{CCl}_4$  should turn pink which indicates iodine is being extracted. Separate  $\text{CCl}_4$  from the aqueous solution and add 5 ml of fresh  $\text{CCl}_4$ . Shake and separate again. Repeat this extraction until no more pink color appears in the  $\text{CCl}_4$  layer. Add 1-2 ml of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and 5 ml of  $\text{CCl}_4$  and shake. This will reduce  $\text{IO}_3^-$  to  $\text{I}_2$ . Repeat extraction once again until no more pink appears in the  $\text{CCl}_4$  layer. Combine all  $\text{CCl}_4$  layers and measure the absorbance at 515 nm using the spectrophotometer.

Place  $\text{I}_2$ - $\text{CCl}_4$  solution in clean separatory funnel and add 20 ml 18 M $\Omega$  water, 2 ml conc.  $\text{H}_2\text{SO}_4$  and 1 ml  $\text{NaHSO}_3$ . Shake until  $\text{CCl}_4$  layer is clear. Do not forget to vent! Discard  $\text{CCl}_4$ . Transfer the aqueous phase to a clean 50 ml centrifuge tube and gently heat to evaporate any  $\text{CCl}_4$  which might still be present. BE CAREFUL NOT TO OVER

HEAT! If all  $\text{NaHSO}_3$  is evaporated, the iodide will oxidize and be released. Add an excess of  $\text{NaCl}$  (about 6-10 mg) and enough  $\text{AgNO}_3$  to precipitate all iodide present and some of the chloride. The presence of chloride will inhibit the formation of Ag-sulfo compounds. Centrifuge to concentrate the  $\text{AgI}$  and  $\text{AgCl}$  and discard supernatant. Add 5 ml of  $\text{NH}_4\text{OH}$  to dissolve  $\text{AgCl}$  and mix well because sometimes  $\text{AgCl}$  is hard to dissolve. Centrifuge again and discard supernatant. Wash with 18 M $\Omega$  water 3 times or until all  $\text{NH}_4\text{OH}$  is removed and dry at 100°C.

Chemical blanks are prepared following this procedure using approximately 6 mg of Banco brand KI. See Appendix A for details on blanks and blank material.

### Discussion

Water from the Aneth field brine was measured for  $^{129}\text{I}/^{127}\text{I}$  ratios. This water is associated with oil from the Aneth field in Utah which has not been tested at this time. Although this measurement can not be used to draw any conclusions about the association between the oil and its associated water, it can test the chemical method for future use. The iodine extracted was approximately 17 ppm I. The ratio measurement obtained was  $4430 \pm 50$  ( $\times 10^{-15}$ ) and the chemical blank ratio was well within the uncertainty limits of the Banco blank (directly precipitated to check background) (see Table 1 for ratio results and Appendix A). The results indicate that the method can be used successfully for formation water samples.

TABLE: 1 RESULTS FROM TAMS RUN

SAMPLE	METHOD	$^{129}\text{I}/^{127}\text{I}$ ( $\times 10^{-15}$ )
Monterey oil	Sodium biphenyl	6200 $\pm$ 2000
San Juan oil	Sodium biphenyl	10,000 $\pm$ 3000
Blank	Sodium biphenyl	381
San Juan oil	Combustion	3465 $\pm$ 47
Blank San Juan	Combustion	223 $\pm$ 62
Blank-1 Miocene	Combustion	60 $\pm$ 47
Blank-2 Miocene	Combustion	48 $\pm$ 27
Aneth field brine	Formation water	434 $\pm$ 50
Chemistry Blank	Formation water	60 $\pm$ 20
Banco blank	Directly precipitated	50 $\pm$ 20

## 2. Crude oil

The crude oil samples used in this study are heavy, highly viscous residues left from high temperature distillation which were carried out in the Texaco laboratories. The first residue is from the Monterey formation, California and contains on the order of 1 ppm I, measured by neutron activation analysis, and the second residue is from San Juan county, Utah, and contains approximately 3.5 ppm I, also determined by neutron activation.

Because of the organic nature of the residue, iodine is believed to be covalently bonded to the carbon. Therefore, the method for extracting iodine should involve breaking of the carbon-halogen bonds. In developing an extraction method for ratio measurements by TAMS, several factors should be kept in mind. The crude oils are expected to have low

$^{129}\text{I}/^{127}\text{I}$  ratios ( $<10^{-13}$ ) and for this reason, carrier, which can sometimes be used in TAMS procedures for low concentration samples (see Appendix A), can not be added or the ratios will be below the detection limit of TAMS. For samples containing around 1 ppm I, about 2.2 kg of petroleum residue must be extracted in order to concentrate 1-2 mg of iodine. Therefore, any method chosen should also have a reasonable sample size to keep a minimum sample preparation time. Another problem that could arise is contamination from the solvents and chemicals used. Once again, since our ratios are so low any trace quantities of iodine from the solvents and chemicals could have high  $^{129}\text{I}$  concentrations, consequently, causing large errors in the ratio measurements.

a. Sodium biphenyl method

Methods of extracting low quantities of halogens from organic material have been successfully carried out using an organic halogen reagent, sodium biphenyl. This reagent is used to break covalent bonds of the carbon and halogen, forming inorganic, water soluble halogen ions.

The reagent has a wide variety of uses[14,15,20-25]; it has been applied to the extraction and detection of trace quantities of fluorine (0.03-500  $\mu\text{g}$ ) in biological materials such as blood serum, body fluids and tissue homogenates, with efficiencies greater than 90% [20,21]. Chlorine and bromine have also been extracted in trace amounts, with up to 99% efficiency, from organic halogen compounds, gasolines and coal derivative products [22,23]. Other studies have been done with various halogen containing organic compounds with similar results [24,25].

The procedure was adapted for the extraction of trace quantities of iodine from petroleum residues, with the following modifications. Due to

the highly viscous state of the residue, it was necessary to use a solvent to dissolve the sample into a homogeneous liquid. The solvent, toluene, was chosen for its solubility effect and for its chemical inertness toward the sodium biphenyl. The methods of detection used in previous studies to determine efficiency proved to be unsatisfactory for low levels of iodine. Iodide electrodes, comparable to fluoride electrodes, and potentiometric titrations, used in previous extractions, did not have stability at the low concentrations typical for our samples. Consequently, an alternative method of detection of total iodine was used. This method involves the redox reaction between ceric and arsenic ions. (see section II.A.2) [14-17]

The sample size for this procedure is 25 g petroleum residue. It then takes about 5 weeks to prepare a AgI sample for TAMS from 2.2 kg of petroleum residue. Contamination from the solvent was a problem with this procedure. Since sodium biphenyl breaks covalent halogen bonds, any iodine impurities bonded to the solvent will also be extracted. The total iodine content of toluene is below our spectrophotometric detection limit in the total iodine analysis, but the  $^{129}\text{I}/^{127}\text{I}$  ratio was found to be above the atmospheric pre-bomb ratio ( $7.2 \times 10^{-10}$ ). It was necessary, therefore, to develop a method to remove iodine from the solvent. The other reagents and chemicals have not had this problem.

#### Apparatus

Distillation apparatus.

Separatory funnels, 250 ml.

#### Reagents.

Sodium biphenyl reagent. This reagent is purchased from Southwestern Analytical Chemical Company in 15 ml vials to eliminate waste and contamination.

Toluene, reagent grade. A purification technique is described below.

2-propanol.

Sodium, metal.

H<sub>2</sub>O. 18 M Ω H<sub>2</sub>O is used throughout the procedure to eliminate any contamination from ions in the water.

Sodium bisulfite (NaHSO<sub>3</sub>), 1M.

Silver nitrate (AgNO<sub>3</sub>), 0.1M

Sodium chloride (NaCl), 23 wt.%

Ammonium hydroxide (NH<sub>4</sub>OH).

#### Iodine reduced toluene

In a 1 liter flask, add 120 ml of sodium biphenyl to 500 ml of toluene. Shake and allow to sit 1 hour. The color should be a dark blue-green; if it is not, add more sodium biphenyl until the color persists. Destroy excess sodium biphenyl with 5-10 ml of 2-propanol. Distill mixture and collect the fraction between 108-110°C. This is an azeotrope of toluene and 2-propanol which can only be separated through chemical means. Add 1-2 g of metallic sodium and allow to sit for 1-2 days. The sodium reacts to destroy the alcohol leaving toluene to be easily separated by a second distillation. This time, the fraction at 110°C is collected.

#### Procedure.

Set up eight, 250ml separatory funnels. Dissolve 25 g of petroleum residue in 70 ml of toluene in a beaker and transfer to a separatory funnel. The best way to accomplish this is to use four, 18ml portions of toluene to dissolve the petroleum. Repeat for all separatory funnels. Add 30 ml (2 bottles) of sodium biphenyl to each and shake vigorously. The mixture should appear black at this point indicating an excess amount

of reagent. For blank samples, i.e. toluene and sodium biphenyl with no residue, the color will be dark blue-green. If color does not persist, more sodium biphenyl should be added. Allow the mixture to sit overnight to ensure a complete reaction. Add 10 ml of H<sub>2</sub>O and gently rock the funnel to destroy excess sodium biphenyl. Do not shake at this point; shaking will cause stable emulsions to form. Vent the funnels to release any gas that has evolved. For blank samples, the destruction of excess sodium biphenyl is clearly evidenced by a change in color from blue-green to colorless. With residue samples, the color change is not obvious, but a lightening of the black color to brown will be evident. Allow the two phases to separate and collect the aqueous layer. The water extraction should be carried out until all I<sup>-</sup> is removed. This is sample dependent and should be adjusted for different samples. For our residue, the extraction is repeated nine more times on each funnel for a total of 100 ml of H<sub>2</sub>O. If emulsions should occur, collect it along with the aqueous phase. This extraction procedure is carried out on enough residue to obtain 2.0 mg I. For samples containing about 1 ppm of I, about 2 kg of the residue is needed.

The aqueous layer is filtered to obtain a clear solution. There should be about 4 liters of solution at this time. Carefully acidify with concentrated H<sub>2</sub>SO<sub>4</sub> to pH 2 and allow any precipitate to form (12-24hrs). Usually about 10-15 ml of acid is used; this depends on alkalinity and amount of solution present. Filter the solution to obtain a clear solution using Whatmann GF-F filters. At this point, a 10 ml aliquot should be removed from the collected solution and tested for total iodine content using the procedure described in section II.A.2. Once the total iodine content is known, the collected solution can be precipitated



as AgI using the steps indicated below.

To ensure all iodine is in the  $I^-$  form, add 1 ml of 1M  $NaHSO_3$ . Stir the solution and allow to sit for 1-2 hours to ensure a complete reaction. For every 1 liter of solution, 12ml of 23 wt%  $NaCl$  is added; this will prevent any Ag-organic and Ag-sulfo complexes from forming. Add a sufficient amount of  $AgNO_3$  to precipitate AgI. A slight excess can be added to account for any error in total iodine analysis, but not more than the molar amount of  $Cl^-$  present. Allow the precipitates to form for about 12-24hrs. Centrifuge to concentrate AgI. Once AgI is collected in a small centrifuge tube, any  $AgCl$  formed is dissolved by adding 5-7 ml of 50%  $NH_4OH$ ; mix well and centrifuge. Wash AgI three times with  $H_2O$  and dry in an oven at  $100^\circ C$ .

### Discussion

Results of some extraction experiments are shown in Table 2. Originally, when 25 g samples were used, an extraction efficiency of up to 90% was found. Due to the long preparation time involved, it was necessary to try and speed up the extraction process by using larger sample sizes. Experiments were conducted with 50 g samples, but with the same amount of toluene (100 ml). Two factors can influence the efficiency: the amount of sodium biphenyl and the number of water washes. If the amount of sodium biphenyl is increased from 30 ml to 45 ml, no significant change occurs in the extraction efficiency (samples: 1,2 and 5,6 in Table 2) of 25 g samples. A decrease in efficiency by more than 20 % is evident, however, going from 25 g samples to 50 g samples (samples: 3,4) which were treated with 30 ml of sodium biphenyl. Although these experiments are incomplete, at present, the lower relative amount of sodium biphenyl in the 50 g

TABLE: 2 IODINE RECOVERY FROM PETROLEUM RESIDUE

Sample	Petroleum (g)	Sodium biphenyl (ml)	Aqueous phase extracted (ml)	Total $\mu\text{g I}^-$	Efficiency (%)
1	25.20	30	173	66.72 $\pm$ 8.65	75
2	25.24	30	186	77.80 $\pm$ 4.70	88
3	50.26	30	192	110.52 $\pm$ 10.42	63
4	50.23	30	212	100.92 $\pm$ 5.88	57
5	25.30	45	190	65.90 $\pm$ 1.90	74
6	25.40	45	243	84.77 $\pm$ 6.04	95

NOTE: 100 ml of toluene was used for all sample extractions.

samples is suspected to be the source of the decreased efficiency. In future experiments, the number of water washes could be increased to see if iodine removal would be increased.

This procedure, even with  $^{129}\text{I}$  reduced solvent, still showed a large contamination problem even though about 90% of the contamination was removed. This then contributed to the large errors associated with the oil ratios shown in Table 1 for this method. The errors associated with these ratios were estimated because the total iodine content of the toluene was not known. Because of the contamination problem, the length of the preparation time, and the amount of mess and hazardous waste produced, an alternative method of extraction was pursued. [26]

b. Combustion method

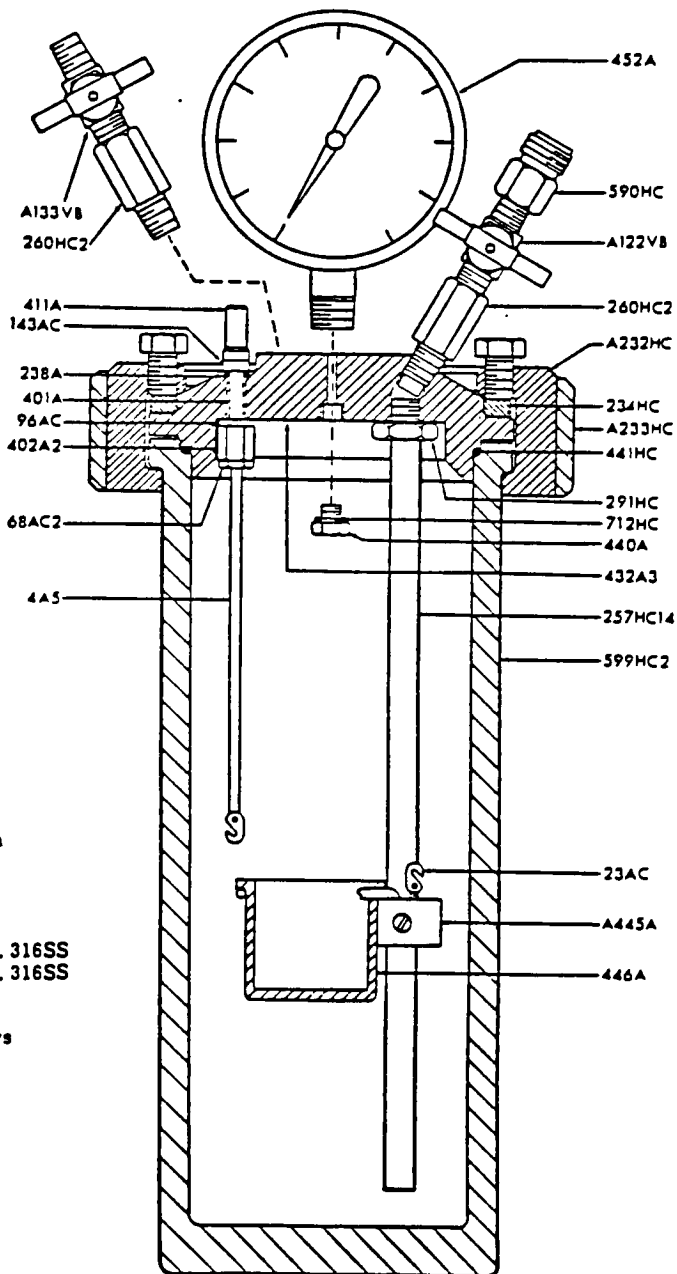
The Parr oxygen bomb\* is designed to oxidize any solid or liquid combustible sample, quickly and completely, without losing any of the sample or its combustion products. All hydrocarbons are oxidized to carbon dioxide and water in the reaction while mineral constituents remain as ash and halogens and other inorganic constituents are released to the vapor or the water.[27]

The combustion bomb used in this experiment is the largest Parr oxygen bomb available. The 1121 combustion bomb has a 10 g sample capacity and uses a charging pressure of 300 psig. It is designed to hold a maximum pressure of 1500 psig. The ability of the 1121 bomb to handle relatively large samples with complete recovery of all liquid and vapor products make it particularly useful in determining trace elements in combustible materials.

The bomb is constructed from a special columbium-stabilized stainless steel (Garpender No. 20cb-3). This stainless steel contains more than twice the nickel used in the more common stainless steels. Its formulation makes it more resistant to  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  generated during combustions. Figure 4 shows the schematic for the 1121 bomb.[27] The bomb head has two valves, a pressure gauge and ignition terminals. The pressure gauge is used only to establish safe working pressures and then is closed off with a plug. The sample is held in a thick walled stainless steel cup supported on a bracket attached to the oxygen inlet. The combustion is initiated by a charge produced from a wire fuse connecting two electrodes. The fuse is 10 cm long and touches the

\* The bomb was manufactured by the Parr Instrument Company, Moline, Illinois.

Figure 4: Schematic for Parr combustion bomb used with permission from Parr Instrument Company. [27]



**PARTS LIST**

- 4A5 Straight electrode, 5"
- A19A7 Oxygen hose assembly with coupling for 1121 bomb
- 23AC Hook electrode
- 68AC2 Lock nut, 303SS
- 96AC Ceramic washer
- A122VB Needle valve, 1/8" NPT (m), 316SS
- A133VB Needle valve, 1/8" NPT (m), 316SS with regulating stem
- 143AC Insulator
- A232HC Split ring, pair, w/cap screws
- A233HC Drop band w/screw
- 234HC Compression ring
- 238A O-ring, Buna-N
- 257HC14 Dip tube, 304SS
- 260HC2 Valve extension
- 291HC Lock nut, 304SS
- 401A Sleeve insulator
- 402A2 Electrode core
- 411A Terminal nut
- 432A3 Bomb head, 316SS
- 440A Gage plug
- 441HC O-ring, 4" O.D., Neoprene
- A445A Cup support bracket
- 446A Combustion cup
- 452A Pressure gage, 3 1/4" dia., 0-3000 psi
- 590HC Adapter for filling connection
- 599HC2 Bomb cylinder, 1850 ml, 316SS
- 712HC O-ring, Buna-N
- 1825 Oxygen filling connection

sample. The electrodes are hooked to an ignition box that will send 115V to ignite the sample. The bomb is sealed using split ring clamps with cap screws and a band around the ring clamps. These parts are not stainless steel and after continuous combustions in water begin to rust.

The literature shows that collecting iodine from organic samples for various analyses has been accomplished using this bomb.[28,29] The iodine concentration in most of their samples has been higher than ppm levels and recoveries were reported to be between 90-100%. The iodine was collected as iodate in an alkaline water phase in the bomb. The method described below is a variation of these methods where sodium bisulfite is added as a reducing agent to keep all the iodine in one state as iodide.

#### Apparatus

1121 Parr Oxygen Bomb.

Sample cup, 41 mm dia. x 35 mm deep 304a stainless steel.

Oxygen tank.

Oxygen filling connection, connection will fit a CGA 540 outlet with a right handed thread.

Beaker, 1-2 liter.

Millipore filters, 0.22 $\mu$ m.

#### Reagents

Sodium bisulfite ( $\text{NaHSO}_3$ ). 1M.

$\text{H}_2\text{O}$ , 18 M $\Omega$ .

Sodium chloride ( $\text{NaCl}$ ), 23wt%.

Silver nitrate ( $\text{AgNO}_3$ ). 0.1M.

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), reagent grade.

Potassium iodide (KI), Banco brand.

### Bomb Preparation

Clean combustion bomb and sample cup well with soap and water. Rinse with H<sub>2</sub>O. Combust 2-3 times with material to be used for sample and discard water. Rinse again with H<sub>2</sub>O. The bomb is now ready for sample combustions.

### Procedure

Place 10.0±0.5 g petroleum in combustion cup and place in the head of the bomb. Connect the 10 cm fuse between electrodes. Put 5-10 ml H<sub>2</sub>O and 1 ml 1M NaHSO<sub>3</sub> in the bomb. Check head gasket and make sure it is in good condition. Moisten it with a few drops of water and then push head firmly into the cylinder. Replace the ring clamps and raise the band from the bottom of the bomb to encircle the rings. Seal the bomb by tightening all the cap screws. (Torque= 25ft-lbs.). Close the outtake valve and hook the oxygen tank to the intake valve. Fill bomb to 300 psig of oxygen. Submerge bomb in cold water and hook up electrodes. Push button briefly on the ignition unit to ignite the bomb. The combustion is complete within a few seconds but the bomb will produce large amounts of heat. Cool the bomb by adding ice to the water as it begins to warm up. Once cooled, remove the bomb and release the pressure through the outtake valve. Loosen cap screws and remove the head. Empty water in bomb to a clean beaker and repeat the combustions in this way until enough petroleum has been combusted to produce 1-2 mg iodine. Check for complete combustion (i.e. no sooty residue) after each combustion. If sooty residue is present, add 50 psig to charging pressure.

Once all water is collected rinse the inside of the bomb and the head with water. Filter the water. Add 4-6 mg chloride (from NaCl solution),

2 ml  $\text{H}_2\text{SO}_4$  and heat until near boiling. Heating will release some excess  $\text{NaHSO}_3$  and addition of  $\text{AgNO}_3$  to a warm solution will help coagulate the precipitate faster. Add enough 0.1 M  $\text{AgNO}_3$  to precipitate all iodide and some but not all chloride. Allow to settle overnight. Centrifuge to concentrate precipitate. Add  $\text{NH}_4\text{OH}$  to dissolve  $\text{AgCl}$  and centrifuge. Rinse with water 3-4 times and dry in oven at  $100^\circ\text{C}$ . Prepare blanks using the above procedure for one combustion with 2 mg Banco potassium iodide in the water in the bomb and 10 g of a petroleum known to be low in  $^{129}\text{I}$ .

## Discussion

Experiments were originally carried out using a 1 g combustion bomb and a compound to simulate the petroleum system (1-iodooctadecane). The vapors were collected either by expelling the gas from the bomb through  $\text{CCl}_4$  or by collection in a liquid nitrogen trap. This would collect any iodine in the  $\text{I}_2$  state present. The water layer in the bomb was also extracted for  $\text{I}_2$  as well as any other higher and lower oxidation states, (primarily  $\text{IO}_3^-$  and  $\text{I}^-$ ). The results showed that no  $\text{IO}_3^-$  or  $\text{I}^-$  were present, only  $\text{I}_2$ . The recovery, at that time, was only 40% by expelling vapors through  $\text{CCl}_4$  and 45% by collecting vapors in the liquid nitrogen trap. We attributed this to losses during the vapor collection (i.e. evaporation of  $\text{CCl}_4$ ). If all iodine can be kept in a non-volatile state (i.e as  $\text{I}^-$ ), it would eliminate the need to collect the gas and in the process increase the recovery. By adding sodium bisulfite to the initial water placed in the bomb, the iodine was recovered as  $\text{I}^-$  and the recovery was increased to 64%. At this point in the method development, it was concluded that a larger bomb was needed to combust more material at one time.

The first step with the 10 g bomb was to find the upper limit of how much petroleum residue could be combusted at one time. The maximum pressure in the bomb after combustion, should not exceed 1200 psig. 19 g of petroleum could be combusted with a maximum pressure of 1100 psig. One problem that had become apparent was leakage around the seal (visible by tiny stream of bubbles from the seal after the combustion). The O-rings supplied with the bomb were Neoprene type rings. The heat produced during these combustions was too high for the O-ring to withstand. Consequently, there was damage to the O-ring and black residue was present on the inside of the split ring seal (Figure 4, A232HC). Various O-rings were tried



including Teflon, viton, and silicone but none would hold up under such intense heat. The problem was eliminated by using 10 g samples as opposed to 19 g and using 300 psig for charging pressure. This produced a maximum pressure of <1000 psig. Silicon O-rings were chosen for their stability at this sample amount.

The combustion method reported in the literature was used to see if iodine could be collected with the reported 90-100% yields. [27,28] Samples in the literature method were organic-iodide compounds and not samples with only trace amounts of iodine. 20 ml 5 M KOH was used in the bomb with 19 g petroleum. The result showed that iodine was in the higher oxidation states (iodate or periodate) but less than 30% of iodine was collected. This might be attributed to the fact that the iodine concentration in these petroleums is much lower than the levels of iodine used in the literature method samples.

Since the literature method did not have a positive effect on the efficiency of the iodine recovery, our original procedure (addition of sodium bisulfite to the bomb) was pursued. Table 3 shows percent yields from extracting iodide from the water phase after combustion with  $\text{NaHSO}_3$ . The extraction of iodide from the water was carried out using hydrogen peroxide as the oxidizing agent and carbon tetrachloride as the extraction solvent, as with the formation waters (see section II.B.1). The yields were between 33-83%. Some of the loss and variation in recovery were thought to be due to the presence of excess  $\text{NaHSO}_3$ . Experiments were carried out on aqueous solutions using known amounts of KI spike and increasing amounts of sodium bisulfite to test this conclusion. Extractions were done in the usual fashion by oxidation of iodide to iodine with  $\text{H}_2\text{O}_2$  and extraction to carbon tetrachloride.

TABLE: 3 EFFICIENCY OF IODINE RECOVERY USING THE COMBUSTION METHOD

Petroleum (g)	Total I ( $\mu$ g)	Recovered I ( $\mu$ g)	% Yield
19.00	57.0	26.6	47
19.39	58.2	24.9	43
19.15	57.5	48.5	83
19.00	57.0	18.9	33
30.90	92.7	59.1	64

TABLE: 4 EXTRACTION OF IODINE IN THE PRESENCE OF VARYING AMOUNTS OF SODIUM BISULFITE

1 M NaHSO <sub>3</sub> (ml)	acid		CCl <sub>4</sub> (ml)	I extracted ( $\mu$ g)	% recovery
	HNO <sub>3</sub> (ml)	H <sub>2</sub> SO <sub>4</sub> (ml)			
0	0	2	4.3	50.96	93.3
1	0	2	5.3	34.90	63.9
2	0	2	4.3	43.0	78.8
3	0	2	4.1	33.6	61.5
4	0	2	3.5	23.9	43.8
4	2	0	4.0	37.9	69.4
4.5	2	0	5.9	31.1	57.0
20	2	0	4.0	11.4	20.9

NOTE: All extractions were carried out using 54.6  $\mu$ g I and 2 ml H<sub>2</sub>O<sub>2</sub>.

Table 4 shows that as NaHSO<sub>3</sub> concentration increases, the amount of iodine extracted decreases. Table 4 also shows that although acidification with HNO<sub>3</sub> can increase the yield compared to acidification with H<sub>2</sub>SO<sub>4</sub>, the efficiency still decreases with increasing amounts of NaHSO<sub>3</sub>. An excess of NaHSO<sub>3</sub> in the bomb, however, is necessary due to oxidation of the NaHSO<sub>3</sub> in the presence of excess oxygen which is

evident from observation of a yellow precipitate (sulfur) forming at the top of the electrodes. A final attempt to increase the yield was by directly precipitating the iodine once combustions were complete; an increase in iodine recovery was expected. Since ratio measurements are independent of concentration, the lower yields would be sufficient to test the method if no increase in recovery was observed.

Isotope measurements were successful using this method. 627.6 g of the San Juan county petroleum was used to prepare a sample. This amount was sufficient to produce 1 mg iodine assuming a 50% recovery. The actual recovery was not determined due to other materials which also precipitated and could not be separated from the silver iodide. These other materials however had no adverse effects on the beam production. Several blanks were prepared using two petroleum samples to check contamination levels. The ratio results and blank measurements are listed in Table 1 in the order they were prepared. Of the three blanks tested, one can see the San Juan blank ratio was much higher than blank-1 and blank-2. Blanks-1 and 2 were prepared from Miocene oil which is believed to be <1 ppm of iodine and have a low ratio about  $10^{-13}$  (this ratio is only estimated). Since 10 g of oil is used to prepare the blank, a correction can be made to account for the counts coming from the oil. For the San Juan blank, the iodine-129 counts coming from the oil can not account for all the counts measured and therefore some of the contamination must be coming from the method (i.e. combustion bomb). Since the other two blanks are within the limits of the Banco blank (Table 1) it was concluded that the contamination was left over from the previous combustions and with proper precautions this contamination can be eliminated. This then was the basis for the bomb preparation method described in this section on page 25.

### 3. Source and reservoir rocks

Table 5 shows the mineral constituents of the source and reservoir rocks associated with the San Juan oil formation.[30] The reservoir rock, a carbonate, contains 97% calcium carbonate, 2% calcium sulfate and 1% silicates. The iodine and uranium concentrations were determined by neutron activation to be 9 ppm I and 3 ppm U. The assumed source rock is another carbonate with 67% carbonate based minerals, 2% sulfur based minerals and 31% silicate based minerals. The iodine and uranium concentrations are 4.6 ppm and 3.0 ppm, respectively. Iodine in these rocks was originally expected to be imbedded in uranium minerals, chemisorbed on Fe or Al hydroxides, precipitated as a metal iodide salt (Pb or Hg in the deposit) or located at crystal boundaries or fluid inclusions. Due to the large ionic size of the iodine molecule, it rarely substitutes in other crystal lattice positions.

Table: 5 MINERAL COMPOSITION FOR ROCK SAMPLES [30]

Mineral Phase	Source Rock %	Reservoir Rock %
Illite (clay mineral)*	17	0
Quartz (SiO <sub>2</sub> )	13	1
Sodium Feldspar (NaAlSi <sub>3</sub> O <sub>8</sub> )	1	0
Calcite (CaCO <sub>3</sub> )	61	97
Dolomite (CaMg(CO <sub>3</sub> ) <sub>2</sub> )	5	0
Pyrite (FeS <sub>2</sub> )	2	0
Siderite (FeCO <sub>3</sub> )	1	0
Anhydrite (CaSO <sub>4</sub> )	0	2

\* Clay minerals have varied chemical compositions which always contain Si.

Methods for extracting iodine from rocks have been accomplished for samples where carrier has been added or for samples which have been irradiated. Some of these methods include alkaline fluxes to release the

iodine in higher oxidation states and mineral acid digestions.[31-34] Since iodine is not expected to be in the crystal lattice, it is suggested that iodine should easily be retrieved from acid digestions.[33] These methods would then need to be modified to extract natural iodine from samples with low iodine concentrations.

Based on the various, possible iodine locations in the rock formation, many of these methods have been experimented with.[31-34] The first method used was an alkaline flux consisting of 2 parts sodium carbonate, 2 parts potassium carbonate and 1 part magnesium oxide. The iodine could then be measured in the aqueous phase using the ceric arsenic analysis (section II.A.2).[31] 2.5 g flux was mixed with 0.5 g rock crushed to 200 mesh and fused at 725°C for 30 minutes. The fusion mixture was then cooled and dissolved in water and a few drops of ethanol on a hot plate. The mixture was then filtered. Iodine was expected to be as iodate in the water. This method proved unsatisfactory for our samples probably due to the low concentration of iodine and small sample size. The second flux method had been developed for meteorite samples and consisted of sodium peroxide and sodium hydroxide to leach iodine from the rock.[32] 10 g of rock crushed to 200 mesh was mixed with 30 g sodium hydroxide and 30 g of sodium peroxide and fused at 650-750°C for 30 minutes. The mixture was allowed to cool and dissolved in water. Depending on the amount of time fused and temperature used, the iodine could either be as iodide in the water or as insoluble periodates in the precipitate. Various temperatures and length of fusing time were used while both phases were tested for iodine by extracting iodine to carbon tetrachloride in a similar fashion as the formation waters (II.B.1). This method was also unsatisfactory for our samples. Flux methods were not pursued any further due to their small sample sizes

and large ratio of flux material to sample material, which could be a potential source of contamination.

HCl, HNO<sub>3</sub>, and HF digestion methods as found in references 33 and 34, also proved ineffective. Iodine was either lost through oxidation, masked by more prevalent reaction mechanisms occurring, or was in the organic material and not being leached. In the case of the HCl digestions, the increased amount of HCl used decreased the iodine extraction. One possible explanation could be the formation of ICl which is not extractable to CCl<sub>4</sub>. With HF digestions, the silicates in the rock were digested, but only with an ideal system (CaCO<sub>3</sub>, Silica, and KI in concentrations comparable to the rock) could the iodine be extracted. The yield was less than 50% and was not repeatable on the actual rock samples. To a small extent, HF oxidized iodide to iodine and was lost. This was observed by the brown color during the dissolution of the ideal system. HNO<sub>3</sub> digestions had a similar oxidizing effect on the iodine which was observed only in the ideal solution. It became apparent in the HNO<sub>3</sub> digestions that the carbonate was also inhibiting the extraction of iodine. To eliminate this interference, NiNO<sub>3</sub> was used to try and precipitate the carbonate before extraction to carbon tetrachloride. This was also ineffective. It was then thought that either the ionic concentration in the solution was too high to allow the extraction of small amounts of iodine or that the iodine was not being released during the digestion. An acid digestion bomb was used to see if the harsher, closed system would be effective in digesting the rock and releasing the iodine in a higher oxidation state (iodate) that would be soluble in the solution and not volatilize. Peroxide, H<sub>2</sub>SO<sub>4</sub> and HF were used in the bomb with iodide spike and heated at 100°C for various amounts of time to see if this oxidation was

possible. The peroxide and  $\text{H}_2\text{SO}_4$  were not strong enough oxidizing agents to oxidize to the higher oxidation state.

At this point a closed system was used to collect the iodine in the vapor state instead of keeping it in the aqueous phase. Iodine collection in this way would be potentially free from contamination and any interfering ions.  $\text{HNO}_3$  was used as the digesting acid since our rock samples were mostly carbonate based. A three neck round bottom flask was used for digestion. Nitrogen was bubbled through the solution through one of the necks and then bubbled through carbon tetrachloride through another neck to collect any oxidized iodine. The nitric acid was added through the middle neck with a syringe. While working with an ideal mixture,  $\text{CaCO}_3$  and KI in the amounts proportional to the carbonate rock, it was found that 30% of iodine could be collected as  $\text{I}_2$  but no more was released even when additional oxidizing agents were used ( $\text{H}_2\text{O}_2$ ). When this was used on the reservoir rock, 10% of iodine was recovered in this way. Although this is a low yield, a sample could be prepared in this way since ratios are independent of concentration. At this time, however, it would be to our advantage to increase this yield. Ion exchange columns were used to try and separate the interferences from the iodine. The resin used was Dowex 1-x8, 20-50 mesh in chloride form. The column was used in the nitrate form. To obtain this form the resin was eluted with 2M  $\text{NaNO}_3$  until no more chloride was present in the water (the water was tested using  $\text{AgNO}_3$ ). The column originally used was 4 inches high and 7mm in diameter. In the digestion of the rock with  $\text{HNO}_3$ , 50 g rock was mixed with an equal volume of water; about an equal volume of  $\text{HNO}_3$  was then used for dissolution. The molarity of nitrate present in this mixture was about 7-8 M. Iodine was not retained on the column due

to the high nitrate concentration, therefore, the mixture was diluted to produce a 1 M or less concentration of nitrate. With model systems (iodide in amounts comparable to the rock,  $<1$  M  $\text{HNO}_3$ , and total volume 200 ml), up to 97% recovery was obtainable, but when the mixture volume was increased to 1 liter which would better model the rock system, the recovery decreased to about 10%. This problem could possibly be eliminated with variations in the column width or height.

It has now been suggested that the majority of the iodine in these oil rocks would most likely be bound in the organic material present. [34] If this is true, fluxes or acid digestions would only be effective for extracting the inorganic iodine and not the organic iodine. It is possible that the method described can extract most of the inorganic iodine. The future of this project then, would be to separate the organic material from the rock using HF digestions, and then combust the organic material using the same procedure as the oil.



### III. TANDEM ACCELERATOR MASS SPECTROSCOPY

#### A. Theory

Mass spectroscopy is an analytical technique designed to separate charged atoms or molecules by their masses based on their motions in electrostatic ( $E/q$ ) and magnetic fields ( $mE/q^2$ ), where  $E$  is the energy,  $q$  is the charge state and  $m$  is the mass of the isotope. This is accomplished essentially by an apparatus consisting of an ion source for the formation of charged atoms or molecular ions, a magnetic analyzer of a few KV to separate ions based on their mass-to-charge ratio, and an ion collector or detector to measure the number of ions per second.[1,2,36]

The TAMS used in this work is located at the Nuclear Structure Research Laboratory at the University of Rochester. A schematic is shown in Figure 5.[37] The sample wheel which holds 7 samples is placed in a cesium sputter ion source where a 35 keV Cs+ primary beam strikes the sample surface at a  $45^\circ$  angle. This will produce a stream of negative ions that are extracted from the source region by a negative potential of about 20 keV applied to the sample. The ions are accelerated to the object aperture and gain energy. A  $90^\circ$  inflection magnet with a mass resolution of 1/180 atomic mass units will analyze the negative ion beam for their momenta. The equation which governs the selection of various isotopes is given by:

$$(Br)^2 = mE/q^2$$

where  $B$  is the magnetic field,  $r$  is the radius of the magnet,  $m$  is the mass of the isotope,  $E$  is its energy and  $q$  is its charge state. Once through the magnet, the ions are decelerated back to 20 keV. A pre-acceleration of the negative ion beam to 150 keV is used to ensure that the injected ion beam is focused at the central terminal where the stripper canal is located.[36]

The ions are then accelerated and injected into the tandem accelerator. The word tandem implies a dual acceleration. In the first half of the acceleration a terminal voltage is set to a value appropriate

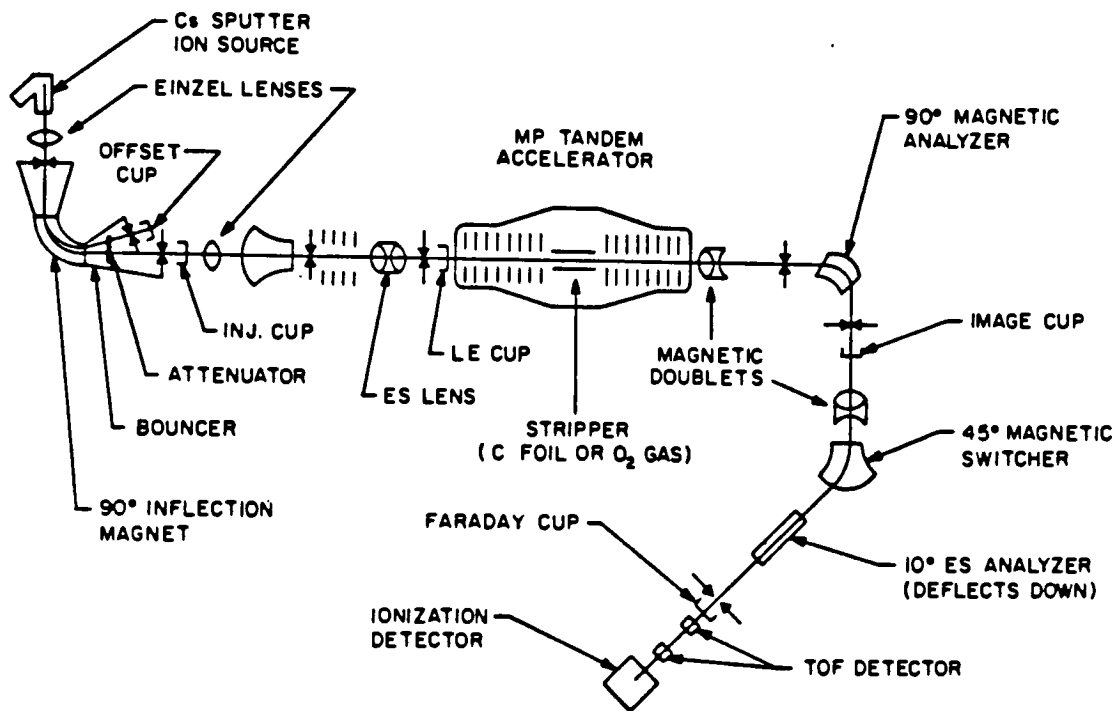


Figure 5: Schematic for TAMS at U of R [38]

for the ion under study. For iodine the terminal voltage is 5 MV. An oxygen gas stripper, which is a differentially pumped gas cell, strips the ions of several electrons and in the process dissociates any molecules. The multiply charged, positive ions are accelerated through the second half of the tandem to ground potential.[36]

Positive iodine ions of charge state 5 are selected by the 90°, 132 cm radius analyzing magnet. Scattered particles and unwanted charge states are eliminated by a 45° deflecting magnet and at Rochester, a 10° electrostatic analyzer then defines the E/q (energy to charge ) ratio. This will remove particles that have different mass but would

otherwise have the same mass-energy product that pass through the magnetic analyzers.[36]

The ions then enter the final detector system. For iodine a time of flight detector coupled with a multiplate gas ionization detector is used to measure the total energy of the iodine ions. The time of flight detector serves as an additional positive-ion mass analysis stage, and is most useful with heavy (slowest) ions such as  $^{129}\text{I}$ . This detector will measure the time it takes a particle to pass between two points. Since the energies are the same, each mass will have a different time of flight.[36]

The isotope ratios are obtained by alternately selecting each stable isotope and measuring its beam current in a removable Faraday cup and then measuring the radioisotope counting rate in the detector. Standards (samples with a known isotope ratio) are measured throughout the run for normalization of the sample ratios and blanks (samples containing no detectable radioisotope) are used to measure the background and contamination. (see Appendix A) In the case of iodine where suitable blank material is not available, the background can not be measured. If the contamination exceeds the level of the Banco blank ( $2 \times 10^{-14}$ ), correction can be made for it.

Acceleration to million electron volt (MeV) energies allows some advantages over conventional mass spectroscopy. The first is that molecular interference can be removed entirely. Ions at MeV energies may be passed through a thin foil or gas where several electrons are stripped off. This process is violent enough to dissociate most molecules. The molecules that survive in charged states higher than  $2+$  are unbound and decay rapidly; if the stripper is followed by a mass/charge analyzer that

selects ions in a charged state of three or greater, only atomic ions will pass through. Analysis of ions at high energies permits measurements of isotopes at abundance ratios far lower than possible at low (keV) energies.[36]

Another significant advantage of accelerator mass spectroscopy is the discrimination against stable atomic isobars. This is accomplished with a combination of techniques. Besides the chemical separation and purification of the element from the sample, one technique for separating isobars relies on the fact that negative ions for some atoms and molecules are unstable. Since the tandem accelerator requires negative ions in the first acceleration stage, many of the interfering isobars are destroyed or are never formed (including N, Mg, KH<sub>3</sub>, and noble gases); this has made possible TAMS of <sup>14</sup>C, <sup>26</sup>Al, <sup>41</sup>Ca, and <sup>129</sup>I. At MeV energies, a particle identification detector can be used for isobar discrimination. These detectors rely on the fact that the rate of energy loss in matter (dE/dx) depends on the atomic number (Z) of the projectile. As Z increases the energy needed for separation also increases. Another isobar separation technique is the stripping of all electrons from an ion at very high energies. This allows complete separation from an isobar of lower Z.[36,37]

TAMS also has advantages over conventional counting methods as well as conventional mass spectrometric and neutron activation methods. The biggest advantage is the detection limit; where conventional methods have a ratio limit on the order of 10<sup>-11</sup> (radio isotope/stable isotope), TAMS has a limit on the order of 10<sup>-15</sup> (see Figure 1 for detection limits). This will allow the measurement of natural ratios of <sup>129</sup>I/<sup>127</sup>I which are on the order of <10<sup>-12</sup>. This detection limit is possible primarily

from the suppression of isotopic background. Background is considered to be any ions which behave like  $^{129}\text{I}$  but are different species and can not be distinguished from the radioisotope being measured. These include unresolved isotopes and isobars in the detector. With TAMS, there is no background from cosmic-ray events as there is with conventional counting. With long lived radioisotopes such as iodine-129, sample sizes for conventional counting techniques would be enormous whereas with TAMS, samples are on the order of 1-10 mg. The actual counting times with TAMS are also much shorter because the ratio is being measured directly using a time of flight detector, rather than having to wait for the natural decay products to be detected. For  $^{129}\text{I}/^{127}\text{I}$  ratios, actual counting time per sample is about 20 minutes. Measurement of an unknown sample takes then about two hours which includes the blank, standard and repeat measurement of the sample.

## B. MEASUREMENTS

The accelerator at UR is almost completely automated. The process is described in a separate paper.[39] The discussion below will be a brief summary of ratio measurements. The computer has control over the following (in order of beam transport): inflection magnet, beam attenuator, (located between the ion source and the accelerator), low-end (LE) Faraday cup, analyzing magnet, and image Faraday cup. The raw data extracted are the stable isotope currents measured at the low-end and image Faraday cups, the counting rate of the radioisotope entering the detector at the end of the beam line and the counting rate of any interference entering the detector. For iodine-129 the interference is the tail from iodine-127.

Wheels are set up to contain two standards, four samples, and one

blank. A cycle is considered to be all the data from beam current measurements and radioisotope counting, needed to obtain one ratio. A sequence is a group of consecutive cycles for a given sample. Each unknown is usually run two or more times, with a total of 2-5 cycles in each sequence depending on reproducibility. The standards are run before and after every 2-3 samples for normalization, which is the correction made for measured ratios. The measured ratio for the standard is usually different from the true standard ratio because of some loss of particles between the image cup and the detector and because non-linear fractionation effects may vary from one sample to the next.

The first step in analyzing the data is to determine the uncorrected ratio measurement for each cycle. This is accomplished using the time averaged radioisotope count rate, the charge state of the ion selected by the analyzing magnet, the elementary charge of the stripped ion, the attenuation of the stable-isotope beam, and the average stable-isotope current measured in the image cup before and after counting the radioisotope. The uncertainty of this number is reported as the absolute error and calculated assuming a Poisson distribution for the counting rate. The currents and other parameters are assumed to have negligible uncertainties compared to the counting rates.

Factors which need to be corrected for before normalization are mass fractionation, background and contamination. Mass fractionation arises from several areas; sample preparation, sputtering and negative ion formation, the terminal stripper, and the beam transport system. In the case of iodine;  $^{129}\text{I}$  behaves as  $^{127}\text{I}$  due to their small relative mass differences (2/127) and consequently no measureable fractionation occurs during sample preparation. Since fractionation is unavoidable in TAMS,

the correction here is due to the fact that iodine-129 does not behave as iodine-127 once in the accelerator and therefore, they will not be transmitted at the same percentage.

Background as stated earlier are any counts which are registered that are false and primarily comes from the tails of other ionic species that the detector cannot distinguish from the radioisotope (tail of  $^{127}\text{I}$ ). The instrument can separate out the background to about  $10^{-15}$ .

Contamination can come from a variety of sources: the environment before or during sample preparation, cross contamination and memory from other samples in the ion source, and residual gas and apertures also in the ion source. During sample preparation, contamination can come from systematic low-level contamination from reagents, glassware, apparatus or environment. These low-level contaminations can be approximately corrected for since it should have the same effect on all the samples, including a blank processed using the sample chemistry. Contamination from the ion source can occur from ionization of the residual gases that may be present (even under high vacuum), and can provide counts if the studied radioisotope is present in the gas. Cross contamination occurs when neutral molecules sputtered from a sample are redeposited on the sample holder and apertures. The error from this contamination can be seen when measuring a blank after measuring a high level sample. This contamination can be assumed to be relatively constant and small if care is taken to avoid large differences in radioisotope concentrations (i.e. measure samples from lower ratios to higher ratios separating them by wheels). Uncertainties of these contamination corrections are usually high systematic errors.

The ratio for each sequence is found by taking the weighted mean of

the cycles for each sample. Errors associated with this ratio are internal and external errors. Internal errors result from combining the statistical errors of each cycle. External errors are the standard deviation of the mean ratios for the cycles. The larger of the two is the uncertainty in the ratio for the sequence.

The final ratio can now be normalized. The normalization factor is found by taking the ratio of the measured standard ratio to the true standard ratio. The weighted average of the normalization factor of the standard measured before the samples and the standard measured after the samples is used to calculate the true ratio of the sample. The uncertainty associated with the normalization factor is the larger of the internal and external errors calculated in the same manner as for the ratio in a sequence. The sample ratio is divided by the normalization factor to obtain the true ratio of the sample and its uncertainty.

The final step is to then calculate the mean average for all the sequences of a sample. For each sample two sequences are normally run on each sample unless a discrepancy occurs then more sequences are measured. The uncertainty associated with this number is once again the larger of the internal and external error as calculated above. This corrected ratio, once again, is determined from a computer program developed by the TAMS group.[39]

The ratio can now be used to calculate significant data by using the age equation:

$$N=N_0e^{-kt}$$

where  $N_0$  is the pre-bomb ratio ( $10^{-12}$ ),  $N$  is the measured ratio,  $k$  is the rate constant ( $k=\ln 2/t_{1/2}$ ), and  $t_{1/2}$  is the half-life.

Corrections can be made to account for the contribution of fission iodine-129 from uranium-238 using the uranium concentration and the cross section for spontaneous fission.



IV. CONCLUSION

Table 1 shows the ratio measurements obtained for the two crude oils and Figure 6 shows the relation between  $^{129}\text{I}/^{127}\text{I}$  ratios measured in the oils and those estimated for associated source and reservoir rocks. The Monterey formation is a relatively young oil and estimated to be about 10 Ma old and has probably not migrated. The oil ratio is somewhat higher than the estimated source rock, but still quite similar. A reasonable assumption is that an isotopic exchange between the source rock and oil occurs during maturation. In the San Juan oil, however the same assumption can not be made. The ratio of the oil is at least an order of magnitude higher than the source or reservoir rock. The most likely explanation of the high ratios is contamination of the oil with atmospheric iodine. These isotope ratios are higher by two to four orders of magnitude than those expected for these oils. One source of this

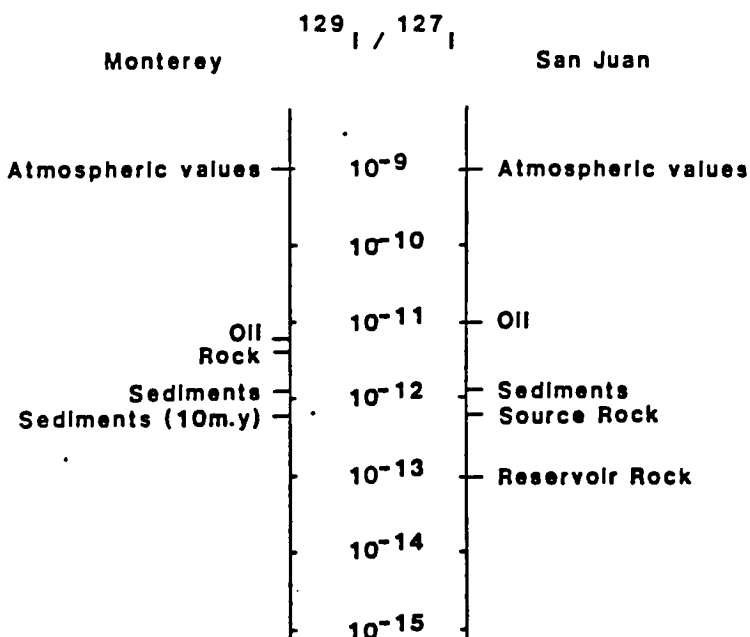


Figure 6: Relationship between ratios for Monterey oil and San Juan oil. [11]

contamination could be during the actual collection of the oil. Surface waters are sometimes used to pump out the oil from a formation and therefore could be mixed with the oil forming stable emulsions. During the processing of these oils de-emulsifiers are used to separate the water from the oil but this does not remove 100 percent of the water. This water then would contain high  $^{129}\text{I}$  concentrations. Another source of contamination could be during the processing of these oils, condensing of the oils to residues, and the containers used for storage (contamination from solvents used to clean the barrels, etc.). The history of the oil once out of the formation is difficult to trace, therefore, much caution has to be used in future sampling procedures. Although no definite conclusions can be made as to the feasibility of using  $^{129}\text{I}$  for dating crude oils, our results show that oils contain sufficient quantities of iodine to make future measurements of this kind worthwhile.[11]

#### SUMMARY

Carrier-free methods of iodine extraction from formation waters and petroleum have been successfully used for ratio measurements. Formation waters contain enough iodine (usually more than 14 ppm) to extract with little problem. There was no observable contamination from this method.

Two methods for extracting iodine from petroleum were used. The sodium biphenyl extraction is able to extract low levels of iodine with up to 90% yields. The 90% recovery of iodine is an advantage of this method but for ratio measurements, contamination from the solvent has inhibited its use. The method's other disadvantages are the production of

large amounts of chemical waste and the length of time to prepare a sample. The alternative method for iodine extraction from petroleum, the combustion method, has up to 50% recovery of the iodine. The petroleum must be combusted in 10 g quantities but the overall preparation time is still shorter than the sodium biphenyl extraction. The biggest advantage of the combustion method is that there is no contamination problem when the proper cleaning techniques are observed. The other advantage is that there is virtually no waste produced.

A method for extracting iodine from rocks has been developed using a closed system, nitric acid digestion and collecting iodine in carbon tetrachloride. At this time, 10 % of iodine can be recovered from the inorganic portions of the rock. The organic portion of the rock is now thought to contain the majority of the iodine and could be recovered by combustion of the organic material.

APPENDIX A:

Blanks are prepared from material which contains little or no radioactive isotope ( $^{129}\text{I}$ ). These blanks can then be used to measure the contamination in chemical methods. If contamination observed in the blank is not too excessive the sample measurement can be corrected. For TAMS, the iodide material chosen for the blank should be out of contact with the hydrosphere for at least, 100 Ma without being exposed to in situ production from  $^{238}\text{U}$ . The material for the blanks was found by observing the  $^{129}\text{I}/^{127}\text{I}$  ratios of all brands of potassium iodide. Actually, the brand is not being tested but the site from which the iodine originated is being tested. Companies generally use different sites for the raw material which will most likely change from shipment to shipment. At the present time the material with the lowest  $^{129}\text{I}/^{127}\text{I}$  ratio is Banco brand KI. The ratio is  $2 \times 10^{-14}$  and is the current detection limit for TAMS.

Carrier is blank material added to a sample which is either too hot (contains a lot of radioactive isotope) and needs to be isotopically diluted or to a sample which has a very low concentration of total iodine and has a high enough ratio to compensate for the dilution.

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