CONF-810682--9

PNL-SA--9141

DE82 003847

MASTER

INTERFERENCE CONTROL IN LOW-LEVEL ^{129}I ANALYSIS

F. P. Brauer
R. S. Strebin Jr.
J. E. Fager
J. H. Kaye

This paper is based on work
performed under Department of Energy
Contract No. DE-AC06-76RLO-1830

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Pacific Northwest Laboratory
Richland, Washington 99352

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MGW

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

INTERFERENCE CONTROL IN LOW-LEVEL ^{129}I ANALYSIS*

F. P. Brauer, R. S. Strebin, Jr., J. E. Fager and J. H. Kaye

Pacific Northwest Laboratory
Richland, Washington 99352

Neutron activation analysis for ^{129}I at levels close to the detection limit requires consideration of radionuclide and nuclear reaction interferences. Low-level gamma-ray spectrometer methods for detection and measurement of interferences have been developed. Procedures which control or eliminate potential ^{129}I measurement errors during pre-irradiation separation, neutron activation, post-irradiation separation, radiation counting and data analysis are needed.

Introduction

Natural and artificially produced environmental ^{129}I levels and ^{129}I migration routes are measured by neutron activation analysis.¹⁻⁶ Some samples require analyses close to the limit of detection. Such analyses require that special attention be directed at control or elimination of interferences.⁷⁻¹⁰

The iodine activation analysis procedure consists of five principle steps:

1. Pre-irradiation separations
2. Neutron activation with a comparator standard

* This paper is based on work performed under Department of Energy Contract No. DE-AC06-76RLO-1830

3. Post-irradiation separations
4. Radiation counting
5. Data analysis

Opportunities exist during each of these steps to control interferences and optimize detection.

The ^{129}I detection limit by neutron activation analysis is determined by several factors:

1. Available neutron flux, time and energy spectrum
2. Decay between neutron exposure and counting
3. Radiochemical iodine recoveries (yield)
4. Counting system sensitivity and selectivity
5. Radiochemical purity of the iodine sample counted
6. Consistency of the counting data and data analysis
7. ^{129}I levels observed in blank analyses

Spurious results can also be generated if ^{130}I is produced during the irradiation from sources other than pre-irradiation ^{129}I . Thus, production of ^{129}I during irradiation can lead to an incorrect result.

This paper discusses the development and integration of various procedure steps required to achieve maximum detection sensitivity and prevention of spurious results from trace interfering radioactivity.

Materials and Methods

Activation analysis of the ^{129}I concentration and the $^{129}\text{I}/^{127}\text{I}$ ratio at nanogram to less than picogram ^{129}I levels requires separation of the contained iodine from environmental and other sample types prior to

neutron exposure. Elements other than iodine which can produce ^{129}I or ^{130}I by neutron exposure must be removed prior to activation. The interfering elements are U, Cs and Te. Uranium must be removed or reduced to very low levels to also prevent production of the other fission product iodine isotopes.

The procedure used for iodine isolation prior to neutron activation is a modification of that of Studier.² A combustion and gas separation procedure has been developed which separates iodine from the sample with little or no detectable uranium, cesium and tellurium present in the iodine fraction.⁸ Experiments have been performed to evaluate these interferences. The sample is spiked prior to combustion with ^{125}I for estimation of the pre-irradiation procedure yield. The addition of ^{125}I spike for yield calculations must also be controlled to maintain the production of ^{126}I by $^{125}\text{I}(n,\gamma)^{126}\text{I}$ at acceptable levels so as not to interfere in the measurement of ^{126}I produced from natural iodine.

The iodine is separated by placing the sample in a quartz combustion apparatus and igniting the sample at high temperature (up to 1000°C) in a stream of oxygen. The off-gases are passed through a small bed of activated charcoal that retains the iodine. The apparatus is shown in Figure 1.

Further purification of the iodine is accomplished by heating the original charcoal trap in flowing nitrogen (up to 1000°C) and collecting the released iodine on a second trap of several milligrams of activated charcoal. The iodine is then removed from the charcoal by heating in a vacuum system, trapping the iodine in a quartz tube at liquid nitrogen

temperature, and sealing the tube to make a quartz irradiation ampoule.

The ^{125}I in the ampoule is determined by gamma-ray spectrometry to estimate the pre-irradiation yield. Typical yields range from 90% to 100%.

It is essential that the activated charcoal and quartz tubing used in the procedure be checked by activation analysis for trace levels of uranium which if irradiated will produce interfering fission product iodine isotopes. Considerable differences in uranium content have been noted in materials from different suppliers.

Quartz ampoules containing the iodine separated from the samples are irradiated with reactor neutrons. Comparator standards containing known ratios of ^{125}I , ^{127}I and ^{129}I are irradiated with each set of samples.⁶ Natural iodine (^{127}I) and spike iodine (^{125}I) in separate ampoules are also irradiated as necessary to check the production of interferences for specific reactor irradiation conditions.

The neutron capture reactions used for the iodine activation analysis are:

Interfering reactions include:

The neutron flux density and length of the irradiation must be controlled to maximize ${}^{130}\text{I}$ production from ${}^{129}\text{I}$ but minimize the production by ${}^{127}\text{I}(n,\gamma){}^{128}\text{I}(n,\gamma){}^{129}\text{I}(n,\gamma){}^{130}\text{I}$. The production of ${}^{126}\text{I}$ by ${}^{127}\text{I}(n,2n){}^{126}\text{I}$ has an effective threshold energy of 11.0 MeV and can be controlled by the irradiation position selected to reduce or enhance the high energy neutron flux density.

Irradiation facilities utilized in this study are located at the Hanford N reactor and the Washington State University (WSU) Nuclear Radiation Center reactor. Available thermal neutron flux densities usually range

from 10^{12} to 10^{14} $\text{cm}^{-2} \cdot \text{s}^{-1}$. Irradiation times normally range from eight to twenty-four hours although both longer and shorter irradiations have been used.

Radiochemical separations of the irradiated iodine from other radioactivity is necessary for maximum analysis detectability. The major interference which must be completely removed at this step is ^{82}Br . A combination volatilization and solvent extraction procedure has been developed for this separation.

Following irradiation the quartz ampoules are cleaned, frozen with liquid nitrogen and crushed into a reaction vessel containing ^{125}I tracer, a dilute H_2SO_4 solution of iodine and bromine carriers, and $\text{Na}_2\text{S}_2\text{O}_5$ (sodium pyrosulfite). The bromide and iodide ions are then oxidized to bromine and iodate by the addition of KMnO_4 and the bromine distilled from the solution. The iodate remaining in the reaction vessel is reduced to iodide with $\text{Na}_2\text{S}_2\text{O}_5$ and then oxidized to iodine with H_2O_2 . The iodine is distilled from the reaction vessel into a $\text{Na}_2\text{S}_2\text{O}_5$ solution. The iodine fraction is further purified by oxidation with H_2O_2 and extraction into CCl_4 followed by back extraction with $\text{Na}_2\text{S}_2\text{O}_5$ solution. A sensitive coincidence gamma-spectrometric procedure is used to monitor the ^{82}Br separation.¹¹ The extractions are repeated as necessary for bromine decontamination. The iodine is finally precipitated as AgI and mounted on thin plastic scintillators for low-level, beta-gated gamma-ray spectrometry.¹²

The ^{126}I , ^{128}I and ^{130}I activities produced in the sample and comparator standards during irradiation are estimated by gamma-ray

spectrometry from several spectra collected over a period of time to obtain half-life information. Low-level, beta-gated, multiple gamma-ray coincidence spectrometric techniques⁷ are used when required to measure very small amounts of activity and to discriminate against interfering activities such as ⁸²Br and fission produced iodine isotopes.

Detection systems used for the gamma-ray spectrometric measurements include coaxial and well-type Ge detectors and beta-gated well-type NaI(Tl) detectors. Some of the well-type NaI(Tl) detectors are multisegmented for gamma-ray coincidence spectrometry. A beta-gated Ge detector system is used for low background, high resolution gamma-ray spectrometry. The ¹²⁵I measurements required for estimation of the chemical yield of the sample iodine and for measuring the amount of the ¹²⁷I and ¹²⁹I in the irradiated comparator standard⁶ are performed with well-type Ge spectrometry systems.¹³

Calculation of the radioactivity levels from the counting measurements is dependent on the measurement device. Both gamma-ray energy and decay data are utilized. Data from high resolution Ge spectrometry is used to evaluate the radiochemical purity of the measured sample and for determination of the amount of the major radionuclides. A weighted least-squares computer routine¹⁴ is used to analyze the sequential NaI(Tl) spectra based on the expected or determined radionuclide mixture. Dedicated small computer facilities are used to supply rapid and timely results so that problems can be quickly recognized and corrected by additional chemistry or counting.

The data-handling programs outlined by Brauer and Fager¹⁵ are used for calculation of analytical results from the sample and standard activity ratios and for preparation of final data tabulations. Corrections are made for interferences, chemical yield, laboratory blanks and sampling blanks where applicable. The results obtained are the ^{127}I and ^{129}I concentrations per unit amount of sample and the $^{129}\text{I}/^{127}\text{I}$ ratio. Corrections are made for laboratory and sampling blanks.

Results and Discussion

Interference control requires detailed attention throughout the procedure. Clean laboratory conditions are required especially during pre-irradiation processing to prevent sample contamination. Separate laboratories have been found desirable for processing environmental level samples and samples from or near ^{129}I sources in order to prevent cross-contamination. Clean-room laboratories are used for low-level samples. Pre-irradiation combustion laboratory equipment is cleaned prior to use by heating to 1000°C with oxygen flow. Spikes are blanked before use.

The ^{125}I spike used for estimation of the pre-irradiation yield is kept to less than 10 Bq to keep production of ^{126}I from ^{125}I much below that produced from sample ^{127}I . After irradiation up to 10^4 Bq of ^{125}I is added for post irradiation yield determination to assure detection in the presence of ^{126}I produced from the sample. When possible coincidence spectrometry 12, 16, 17 is used for ^{125}I measurements to give absolute values and eliminate errors due to counting geometry and self-absorption.

Methods for detection and control of interferences resulting from irradiation of U, Cs and Te impurities in the iodine samples have been developed.⁹ Gamma-ray spectrometric analysis of the radiochemically purified iodine after irradiation provides a sensitive test for fission product isotopes from uranium.

Activation of ^{130}Te also will produce ^{131}I . Thus ^{131}I is a sensitive indicator of interference from both U and Te. The abundance of other iodine fission products signals the presence of uranium impurities. Radioiodine detection and isotopic identification at levels less than 0.01 Bq is performed with beta-gated NaI(Tl) or Ge spectrometry.

Radiochemical analysis of the residual radioactivity in the distillation pot after iodine separation has also been used to estimate interference levels. Both irradiated Te and Cs from iodine analysis irradiations have been measured with their ^{127}Te and ^{134}Cs activation products. The relationships between measured ^{131}I , ^{127}Te , ^{134}Cs activities and spurious ^{129}I results have been determined for typical 16 hour irradiations at the Hanford N reactor (thermal neutron flux density of $10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$) by irradiation of Te and Cs. The amounts required to produce ^{130}I equivalent to 1 pg of ^{129}I are 3.3 μg Te or 0.5 mg Cs. Amounts of Te and Cs determined in typical irradiation ampoules from radiochemical measurements are shown in Table 1. The equivalent ^{129}I is also shown. The ^{129}I values should be compared with the ^{129}I detection limit by neutron activation analysis of about 0.01 pg. Interference from Cs is very unlikely. Interference from Te is possible but can be routinely monitored by observing ^{131}I levels in the separated iodine.

Multiple capture of neutrons by natural iodine ^{127}I produces ^{129}I and ^{130}I during irradiation. This limits the improved sensitivity that can be obtained by increasing the exposure time and neutron flux. Neutron exposure conditions are selected on the basis of expected stable iodine content of given sample types in order to limit the correction required due to multiple capture reactions to less than 10%. Natural iodine is irradiated with sample ampoules as necessary to determine the correction based on the sample ^{127}I content. About 0.002 pg of ^{129}I equivalent are produced per μg of ^{127}I for a 16 hour N reactor irradiation at $10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$. Samples which contain milligram quantities of ^{127}I are irradiated at lower flux density or for shorter times. A factor of ten reduction in flux density reduces the correction by a factor of over one hundred to where it is insignificant for most thyroid and similar high natural iodine samples.

Interference from fission product iodine isotopes in the measurement of ^{130}I has been a more serious problem. Less than 1 pg of uranium is required to produce fission product iodine in amounts which can interfere with detection of low-level amounts of ^{130}I equivalent to 0.1 pg of ^{129}I . A number of NaI(Tl) and Ge(Li) counting systems have been evaluated for ^{130}I measurements.⁷ The Ge(Li) systems are superior for detection and discrimination against interferences such as bromine and fission product iodine isotopes. However, they lack sensitivity for very low-level measurements and for measurements in the presence of ^{126}I produced from samples high in natural iodine. Beta-gated NaI(Tl) gamma-ray coincidence spectrometric systems have been found to be the most sensitive measurement systems with good discrimination against traces of bromine or fission

product iodine radioactivities. Measurements with both beta-gated Ge and beta-gated NaI(Tl) on each sample yield the best complete data set required for low-level analysis.

Table 2 lists major gamma-ray energies for evaluation of ^{130}I gamma-ray spectrometric measurement systems. Large well-type NaI(Tl) detectors provide high efficiency for ^{130}I sum peak measurements as shown in Figure 2. Complete radiochemical separation of ^{82}Br is required for low-level measurements since ^{82}Br has a higher energy sum peak than ^{130}I . The sum peak energies listed on Table 2 also show the need for the absence of fission product ^{132}I and ^{135}I which will interfere with the ^{130}I sum peak measurements. Some discrimination against ^{135}I is achieved with multi-gamma-ray coincidence systems. The well-type NaI(Tl) detectors also permit the measurement of ^{130}I in the presence of major ^{126}I since a ^{130}I sum peak is at a higher energy and much more abundant.

High resolution Ge gamma-ray spectrometry has been found most useful for measurement of ^{125}I , ^{126}I , ^{128}I and ^{131}I required in the analysis. The use of well-type detectors increases the efficiency for these isotopes but not for ^{130}I as shown in Table 3. The Ge spectra are also very useful for identification of trace amounts of ^{132}I , ^{133}I and ^{135}I which may not be apparent from the NaI(Tl) spectra or from radioactive decay analysis at low counting rates. Less than a total of 100 counts may be observed in the NaI(Tl) ^{130}I sum peak region over several half-lives. The Compton from ^{126}I also interferes with ^{130}I detection by Ge systems. Figures 3 and 4, the Ge spectra for ^{126}I , ^{128}I and ^{130}I , show that trace levels of ^{130}I can not be detected in the presence of excess ^{126}I activity. At

low ^{126}I levels beta-gated Ge spectra are very useful in differentiating fission product and ^{130}I activities at levels of less than 0.01 Bq. A typical N reactor sample irradiation produces 1 Bq of ^{130}I per 0.2 pg ^{129}I . Environmental ^{129}I levels are often less than 0.02 pg ^{129}I per gram of sample. Thus high measurement sensitivities are required.

Computer-assisted sample and data analysis has been found more reliable and capable of correcting for interferences and errors than complete computer data analysis. This is especially important when systematic as well as random errors are of concern. Both gamma-ray energy and decay information from several different measurement systems are used. Since the presence or absence of interference varies between analyses, iteration is used to determine the best data fit for each analysis. Evaluation of the results is based on several models for the expected radionuclide mixture. At low total counts for ^{130}I the basic uncertainty is not the count rate determination but the assurance that the measured activity was ^{130}I . Consideration of all interferences supplies confidence in this determination and in the final ^{129}I estimate.

Acknowledgements

The authors would like to acknowledge the assistance of past and present members of the Analytical and Nuclear Research section who have contributed to the development of our ^{129}I analysis capability. We would also like to acknowledge discussions with Dr. M. H. Studier who identified many potential interferences in his original development of ^{129}I neutron activation analysis.

References

1. B. C. PURKAYASTHA, G. R. MARTIN, Can. J. Chem., 34 (1956) 293.
2. M. H. STUDIER, et al., J. Inorg. Nucl. Chem., 24 (1962) 755.
3. R. R. EDWARDS, Science, 137 (1962) 851.
4. B. KEISCH, R. C. KOCH, A. L. LEVINE, Modern Trends in Activation Analysis, Texas A&M University, College Station Texas, (1965) 284.
5. F. P. BRAUER, J. D. SOLDAT, H. TENNY, R. S. STREBIN, JR., Environmental Surveillance Around Nuclear Installations II, IAEA, Vienna (1974) 43.
6. F. P. BRAUER, R. S. STREBIN, JR., Nuclear Activation Techniques in the Life Sciences, IAEA, Vienna (1979) 27.
7. F. P. BRAUER, J. H. KAYE, IEEE Trans. on Nucl. Sci., NS-21 (1974) 446.
8. F. P. BRAUER, H. TENNY, ¹²⁹I Analysis Methodology, Pacific Northwest Laboratory Rep. BNWL-SA-5287 (1975).
9. J. H. KAYE, et al., Radioelement Analysis Progress and Problems, Ann Arbor Science Publishers, Ann Arbor (1980) 165.
10. H. L. ROOK, et al., Anal. Chem., 47 (1975) 1557.
11. F. P. BRAUER, R. E. CONNALLY, H. G. RIECK, JR., Trans. Am. Nucl. Soc., 15 (1972) 153.
12. F. P. BRAUER, J. H. KAYE, R. E. CONNALLY, Radionuclides in the Environment, American Chemical Society, Washington, D. C., (1967) 231.
13. F. P. BRAUER, W. A., MITZLAFF, IEEE Trans. on Nucl. Sci., NS-25 (1978) 398.
14. W. L. NICHOLSON, J. E. SCHLOSSER, F. P. BRAUER, Nuclear Instr. Methods, 25 (1963) 45.
15. F. P. BRAUER, J. E. FAGER, IEEE Trans. on Nucl. Sci., NS-23 (1976) 743.
16. J. S. ELDRIDGE, P. CROWTHER, Nucleonics, 22 (1964) 56.
17. J. G. V. TAYLOR, Standardization of Radionuclides, International Atomic Energy Agency, Vienna (1967) 341.

Table 1

Production of Equivalent ^{129}I from Te
and Cs in Typical Irradiated Ampoules

^{127}Te	(β^- counts/min)	600 to 70,000
^{129}Te	equivalent (μg)	0.006 to 0.7
^{129}I	equivalent (pg)	0.002 to 0.2
^{131}I	(γ counts/min)	1 to 2000
^{129}Te	equivalent (μg)	0.0002 to 0.3
^{129}I	equivalent (pg)	0.00006 to 0.09
^{134}Cs	(γ counts/min)	500 to 50,000
^{134}Cs	equivalent (ng)	0.25 to 25
^{129}I	equivalent (pg)	0.5×10^{-6} to 50×10^{-6}

Table 2

Principle Gamma-Rays of Radionuclides Which May
Be Present in ^{129}I NAA After Radiochemistry

Nuclide	T 1/2	X-ray or Gamma-ray Energy (keV)	Abundance (%)	Highest Major Gamma-ray Sum Energies (keV)	Abundance (%)
^{125}I	59.7d	35.5 31.0 27.5 27.2	6.67 25.8 74.2 39.8	66.5	6.
^{126}I	13.0d	754.0 666.0 389.0	3.9 32.6 35.40	1420 2040	4.6 0.007
^{128}I	25min	443.0	17.5	970 1580	1.9 0.012
^{129}I	$1.6 \times 10^7\text{a}$	39.6 34.4 33.6 29.8 29.5	7.5 2.4 10.8 37.1 20.0		
^{130}I	12.4h	1157.0 739.0 668.0 536.0 418.0	11.4 80.8 94.0 99.8 32.6	1940 2360 2810	48. 46. 0.09
^{131}I	8.0d	364.0	82.4	720	2.2
^{132}I	2.3h	954.0 773.0 668.0	18.5 78.0 100.0	2840 3390	12.8 0.003
^{133}I	20.8h	530.0	89.0	1590	0.4
^{135}I	6.6h	1261.0 1132.0 547.0	34.9 26.8 86.4	2230 2260 2470	7.4 4.7 0.14
^{82}Br	35.3h	1475.0 1317.0 1044.0 828.0 776.0 698.0 619.0 554.0	17.0 27.0 28.0 24.3 83.2 28.0 39.6 72.5	2650 2830	98.6 1.4

Table 3

Counting Efficiencies for ^{130}I

^{130}I Energy (keV)	Photo Peak Counts/Disintegration			
	Well Ge(Li)	Large Coaxial Ge(Li)	Well NaI (TI)	
			13 cm Dia.	23 cm Dia.
418	0.012	0.012		
536	0.039	0.033		
668	0.028	0.026		
739	0.020	0.020		
1157	0.0039	0.0028		
1206 Sum	0.0064			
1276 Sum	0.0043			
1408 Sum	0.0033			
1694 Sum	0.0009			
1826 Sum	0.0006			
1945 Sum	0.0008			
2362 Sum	0.0002		} 0.24	0.56

FIG. 1 DIAGRAM OF SAMPLE COMBUSTION APPARATUS

FIG. 2 ^{130}I SPECTRUM IN WELL-TYPE NaI (TI) DETECTOR

FIG. 3 ^{128}I + ^{126}I SPECTRUM IN WELL-TYPE Ge(Li) DETECTOR

FIG. 4 ^{130}I SPECTRUM IN WELL-TYPE Ge(Li) DETECTOR

LIST OF FIGURES

1. Diagram of Sample Combustion Apparatus	17
2. ^{130}I Spectrum in Well-Type NaI (Tl) Detector	18
3. $^{128}\text{I} + ^{126}\text{I}$ Spectrum in Well-Type Ge (Li) Detector	19
4. ^{130}I Spectrum in Well-Type Ge (Li) Detector	20