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**THE DETERMINATION OF
INORGANICALLY BOUND IODINE-131
IN URINE**

by

William D. Fairman

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William D. Fairman

Industrial Hygiene and Safety Division

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INTRODUCTION

If iodine-131 is the only gamma-emitting nuclide present in a urine sample and a gamma spectrometer is available, this nuclide can be directly measured in the sample without applying chemical separation procedures. On the other hand, if other gamma emitters are present with energies that might interfere in the measurement of the iodine-131, or if a spectrometer is not available and if beta absorption and/or half-life studies are not feasible or prove inconclusive, then a chemical separation that is specific for iodine must be applied.

This paper describes a procedure that is specific for iodine occurrence as inorganic iodide. Although the basic chemistry of the individual steps of the procedure is not new, the procedure as a whole is, also, the incorporation of these individual steps into a unified procedure has yielded some interesting results which, when fully developed beyond that reported here, may prove of more potential value than the procedure.

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ABSTRACT

Inorganically bound iodine-131 is separated from other urinary constituents by ion exchange on a silver chloride column. After removal as iodic acid from the column by acidified chlorine water, the iodine is subjected to two oxidation-reduction solvent-extraction cycles and finally precipitated as silver iodide. The mounted precipitate is beta and/or gamma counted. Chemical and radiochemical yields are $87.2 \pm 1.5\%$. Total time for the procedure (exclusive of counting time) is approximately two hours for a single sample. Tracer interference experiments show that silver, chloride, bromide, and mercury exchange onto the silver chloride, but these elements are removed in the elution and extraction steps. The other elements studied - cadmium, cerium, antimony, ruthenium, tellurium, molybdenum, and technetium - do not exchange onto the silver chloride.

INTRODUCTION

If iodine-131 is the only gamma-emitting nuclide present in a urine sample and a gamma spectrometer is available, this nuclide can be directly measured in the sample without applying chemical separation procedures. On the other hand, if other gamma emitters are present with energies that might interfere in the measurement of the iodine-131, or if a spectrometer is not available and if beta absorption and/or half-life studies are not feasible or prove inconclusive, then a chemical separation that is specific for iodine must be applied.

This paper describes a procedure that is specific for iodine occurring as inorganic iodide. Although the basic chemistry of the individual steps of the procedure is not new, the procedure as a whole is; also, the incorporation of these individual steps into a unified procedure has yielded some interesting results which, when fully developed beyond that reported here, may prove of more potential value than the procedure.

Since the bulk of the urinary iodine is present as inorganic iodide - the organic iodine comprising a maximum of 20% of the total iodine present⁽¹²⁾ - it was decided to develop a rapid specific procedure for the determination of inorganic iodide only. The total iodine-131 present can be estimated by using a correction factor (weighted on the "safe" side - i.e., assuming that the amount of organic iodine present is 20%).

Organic iodine in biological material has been separated from and/or converted into inorganic iodide by: adsorption on ion-exchange resin, followed by alkaline elution;⁽¹²⁾ alkaline ashing;^(3,10) acid-permanganate oxidation prior to oxalate reduction and distillation;^(19,30) melting with a flux of sodium peroxide and ethylene glycol;⁽²⁶⁾ and chloroacetic acid precipitation.^(7,9,29)

Among the inorganic iodide separations that have been applied to biological and/or nonbiological samples are: ion-exchange on synthetic resins;^(4,7,11,20,29) coprecipitation with, or ion-exchange on, silver chloride;^(2,6,12,13,22,23) isotopic exchange on silver iodide;^(15,18) and solvent extraction.^(3,14,28)

The classical gravimetric method for the determination of iodine involves the precipitation of the iodine from acidic solution as silver iodide. If bromide and chloride are present, however, they will also be precipitated. If, instead of silver, palladium(II) is used as the precipitating ion, the iodide can be precipitated independently of the bromide and chloride.

Before precipitation, the iodine might also be separated from the other halides by oxidation of the iodide to free iodine by nitrous acid (the other halides not being oxidized), and extraction of the iodine into carbon tetrachloride or other solvent.

The rapidity and potential selectivity of the anion exchange of iodide on silver chloride, and of the isotopic exchange on silver iodide, made these two techniques appear most promising for investigation.

The ready availability of precipitated silver chloride, and the potentially greater ease with which the exchanged iodide could be eluted from the silver chloride, determined the initial decision to pursue this method.

Because of the rapidity of the iodide-chloride exchange, relatively large-size (20-40 mesh) "granules" of silver chloride can be used, resulting in high flow rates for the sample solution. A large column of silver chloride can be prepared easily (see Appendix D and Figure 1) and is economically feasible, since the iodide can be removed easily by acidified chlorine water, which simultaneously regenerates the silver chloride.

Figure 2 shows that the column size (which retains approximately 20 ml of liquid) utilized is more than adequate for the amount of iodide carrier (20 mg) and sample volume (300 ml) routinely used. To obtain the photograph, five times the normal loading of carrier and sample volume were used; yet the iodide is still confined to the uppermost portion of the column, with no leakage or washout of added carrier or tracer iodine-131. With the flow-rates used (25-30 ml/min), the average residence time of the flowing liquid on the column is between one-half and one minute, an indication of the fast rate of exchange obtained.

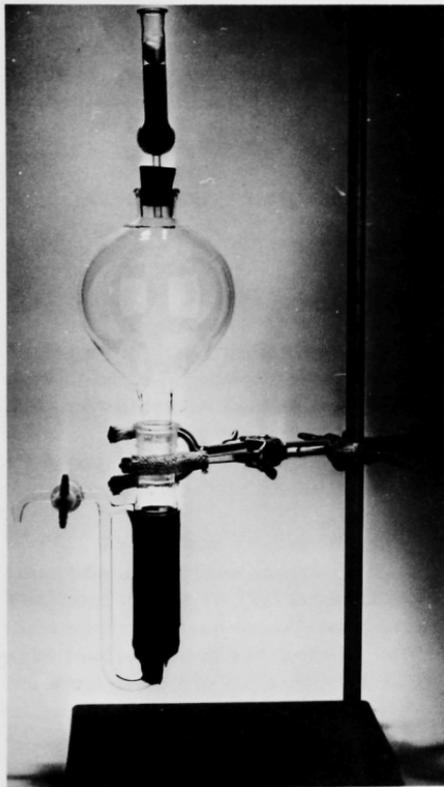


Figure 1. Silver Chloride Column

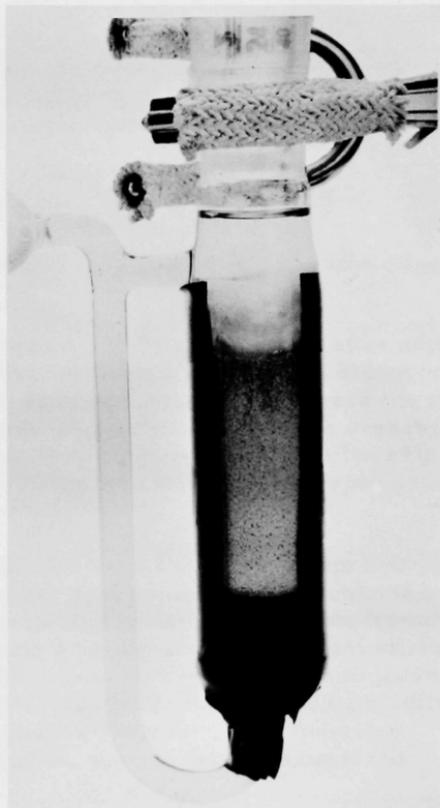


Figure 2. Silver Chloride Column
Partially Exposed to Show
Exchanged Carrier Iodide
on Upper Portion of Column

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An acidified urine (0.1 N in sulfuric acid) is used to ensure homogeneity of the sample, to prevent clogging of the column with neutral or alkaline insolubles present in urine salts, and to minimize the dissolution and fracturing of the silver chloride, which might result from the presence of ammoniacal agents in the sample solution.

A double oxidation-reduction, solvent-extraction cycle⁽⁵⁾ is incorporated into the procedure as an additional decontamination step and as a volume-reduction step. The simultaneous use of two organic solvents is applied in these extractions to effect all extraction steps in a single vessel.⁽²⁴⁾

To obtain the iodide in a form satisfactory for beta counting, the iodide is precipitated as the highly insoluble silver salt, which precipitate is then mounted on a planchet for counting.

PROCEDURE

The detailed procedure is presented in Appendix A; only an outline of the procedure will be given here.

The urine sample (300 ml) is made 0.1 N in sulfuric acid after adding 20 mg of iodide carrier and is then passed through a 20-40 mesh silver chloride column (liquid retention volume of approximately 20 ml), where the inorganic iodide is exchanged with the chloride on the column. The exchanged iodide is then oxidized off the column as iodic acid by using acidified chlorine water as eluting agent; at the same time, the eluting agent rejuvenates the chloride content of the column.

The iodate is then formed by alkaline digestion with sodium hydroxide and reduced to free iodine and/or iodide by hydroxylamine hydrochloride. The free iodine is extracted into benzene. Any iodide and triiodide formed in the reduction step is oxidized to free iodine by nitrous acid (sodium nitrite in acid medium) and extracted. After carbon tetrachloride is added to increase the density of the organic phase, the extracted iodine is reduced by bisulfite to iodide and stripped into an aqueous phase. This oxidation-reduction, solvent-extraction cycle is then repeated for further purification of the iodine.

The stripped iodide is finally precipitated as silver iodide from acid solution by adding an excess of silver ions. The dried precipitate is then mounted on a planchet and beta- and/or gamma-counted.

Total time for the procedure (exclusive of counting time) is approximately two hours for a single sample.

RESULTS AND DISCUSSION

The radiochemical recovery has been determined to be identical with the chemical recovery, showing that satisfactory exchange has occurred between the iodine-131 iodide tracer and the carrier iodide. "Recovery" will, subsequently, mean both chemical and radiochemical recovery. Table I shows the recoveries obtained from 20 urine samples initially used in the procedure, in 1961. The average recovery is $87.2 \pm 1.5\%$, the range of results being between 83.3 and 89.7%. In the past two and a half years, the procedure has been used by the ANL Bioassay Group to analyze approximately 300 urine samples for iodine-131, using two silver chloride columns. The silver chloride in these columns has been periodically backwashed, but not renewed in this time period. A recent examination of the columns has shown no apparent change in the silver chloride, although approximately 45 liters of acidified urine, 15 liters of acidified chlorine water, and 60 liters of 0.1 N sulfuric acid have passed through each column. The apparent stability of these columns is shown by the fact that the recoveries for the most recent 50 samples averaged 88.0%. The columns evidently have little, if any, memory effect, as blank samples remain at background count rate levels and do not increase after active samples have been processed through the columns. Since blank samples beta-count at essentially instrumental background count level (0.3-0.5 cpm) and with an iodine-131 efficiency of approximately 30% (depending on the weight of the silver iodide precipitate), the limit of detectability for this procedure is less than 50 dpm total iodine-131 in 1.5 liters of urine. This is based on the following assumptions: (a) a 300-ml sample is used; (b) less than 20% of the iodine occurs in an organic or nonionic-iodide form (12); (c) a count rate of 2 cpm is considered positive; and (d) a recovery of 87% is obtained.

Table I

CHEMICAL AND RADIOCHEMICAL RECOVERIES FOR IODIDE (IODINE-131) FROM 300-ml URINE SAMPLES

Sample	Chemical and Radiochemical Percent Recovery	Sample	Chemical and Radiochemical Percent Recovery
3864	86.8	4660	86.3
3865	87.7	4661	85.8
3866	83.3	4788	88.2
3960	88.2	4789	88.2
3975	87.2	4790	86.3
4081	86.3	4791	85.8
4082	87.7	4792	85.3
4083	88.7	5587	89.2
4658(A)	86.8	5588	87.2
4658(B)	89.7	5631	89.2
Average = $87.2 \pm 1.5\%$			

To determine the specificity of the procedure for iodine, a series of interference studies was made on elements that possessed chemistry similar to iodine or were representative of various cationic oxidation states and/or fission products. Table II lists the results of these studies.

Table II
INTERFERENCE STUDIES

Isotope	Initial Chemical Form	Exchanges onto AgCl	Elutes from AgCl	Extracts	Precipitates with AgI	Remarks
Ci ³⁶	HCl	> 6% (1 min) > 60% (60 min)	No	No	-(a)	No interference
Br ^{82*}	KBr	~90% (1 min) 99% (5 min)	10% (1 min) 20% (15-30 min)	No	-	No interference
Ag ^{110*}	AgNO ₃	~80% (1 min) ~98% (10 min)	No	No(b)	Yes(c)	No interference
Hg ²⁰³	Hg(NO ₃) ₂	~50% (1 min) ~60% (60 min)	-	-	-	Probably will not elute from AgCl; therefore no interference
Cd ^{109*}	Cd(NO ₃) ₂	No	-	-	-	No interference
Ce ^{144*}	CeCl ₃	No	-	-	-	No interference
Sb ^{125*}	SbCl ₃ and SbOCl	No	-	-	-	No interference
Ru ^{103*}	RuCl ₃	No	-	-	-	No interference
Te-mixture*	Te(NO ₃) ₄	No	-	-	-	No interference
Mo ^{99*}	(NH ₄) ₂ MoO ₄	No	-	-	-	No interference
Tc ^{99m*}	NH ₄ TcO ₄	No	-	-	-	No interference

*Fission product or some other isotope of the same element is a fission product.

(a)-, not studied.

(b)On the basis of two exploratory experiments, there is an indication that a small amount of Ag¹¹⁰ does follow through the extraction procedure if iodide carrier is present, but to a lesser extent if the carrier is absent.

(c)Under the conditions of the iodine procedure, the silver is only partially precipitated because of the presence of an excess of silver from the silver nitrate precipitant.

These interference studies were limited to tracer amounts. Rather than contaminate a silver chloride column, the silver chloride exchange experiments were performed batchwise. The tracer was added to 25.0 ml of 0.1 N sulfuric acid, and then the iodide carrier was added. This solution was contained in a low-actinic, glass-stoppered, 125-ml Erlenmeyer flask (to minimize photolytic effects). A stirring bar and 7.0 g of 20- to 40-mesh silver chloride were then added to the solution, which was stirred at a speed just sufficient to maintain good mixing (partial "suspension") of the silver chloride in the solution. Aliquots (500 lambda) of the supernatant (after rapid settling of the solid) were then removed at various time intervals, the total time of mixing ranging from approximately 0.5 minute to one or more hours. The aliquots were placed into small beakers and counted by gamma spectroscopy, except for the chlorine-36 aliquots, which were beta-counted by liquid-scintillation techniques.

The elution experiments were also performed batchwise and only on those elements which exchanged onto the silver chloride. In this case, after

the tracer had been exchanged onto the silver chloride, the silver chloride was separated from the tracer solution and 50.0 ml of 0.1 N sulfuric acid saturated with chlorine was added to the silver chloride. Again, 500-lambda aliquots were removed at periodic intervals, and gamma- or beta (chlorine-36)-counted.

As is evident from Table II, none of the tracers studied will interfere in the iodine procedure. However, some interesting developments that have come out of these studies are only partially indicated in the table.

Chloride, bromide, and iodide all exchange, as expected, onto silver chloride at varying rates in the presence of iodide carrier. This fact suggested further study on the effects of using

- a) Other alkali halide carriers at varying concentrations,
- b) No carrier,
- c) Other silver halides as exchange media, and
- d) Other insoluble halides as exchange media.

These studies have only proceeded on a limited basis thus far, but the anionic and isotopic exchanges for the various halide tracers fluctuate from "no exchange" to "complete exchange" and at varying rates, depending on parameters a), b), and c) [parameter d) has not been studied]. These studies will be the basis of a separate report.

The exchange rate of mercury-203 suggests the presence of two forms of mercury, or one form exchanging by two different mechanisms, since initially there is a very rapid exchange of approximately half of the mercury (in one minute) and then a slow exchange of only an additional 10% in the next hour.

The relatively rapid exchange of silver-110 onto silver chloride is probably isotopic in nature as has been previously reported^(21,25) for this exchange from nitrate media. It could, however, under the present conditions, conceivably be a surface submicro precipitation phenomenon.

The extraction study with silver-110 also yielded interesting results, as noted in footnote (b) of Table II - namely, that there is an indication that a small amount (a few percent or more) of silver-110 tracer is carried through the extraction portion of the procedure. A simple experiment was conceived to test the possibility that an interfacial phenomenon was involved. Duplicate samples of silver-110 tracer in 30 ml of water were shaken for one minute with three portions of 5 ml of benzene. Duplicate samples of the tracer solution in 30 ml of urine were also made and shaken for one minute with a single 5-ml portion of benzene. In the latter case, as would be expected, a foam was formed. The foam, which was quite

stable under these conditions, separated with the organic phase on separation of the layers. In each of the duplicate samples, 0.2% of the silver was extracted from the water samples (total of three extractions on each); however, 33.5 and 34.6% of the silver was extracted (in a single extraction) from the duplicate urine samples. This experiment provided two extreme interfacial extraction conditions; the results not only tended to substantiate the assumption made that the silver extraction in the iodine procedure is due to interfacial phenomenon, but also provides a further indication of the potential effectiveness of foam extraction as a separation procedure, particularly in the separation of tracer amounts of heavy metals. Conceivably, foams could also be formed with specific exchange properties. The use of foams as gross separation media has been investigated in radioactive waste studies.⁽²⁷⁾ Such use appears particularly attractive in very low-level radioactivity analyses, where large volumes of samples are usually required in order to obtain measurable results. Foam extraction would result in tremendous volume reductions, since foams, although possessing very large surface areas, reduce to minimal volume upon collapsing.

Another result (given in Table III) obtained during development of the iodine procedure was in the preparation and standardization of iodine-131 solutions. Iodine-131 solutions were prepared in reducing and nonreducing (but not oxidizing) media - 0.005 M sodium sulfite and 0.01 M hydrochloric acid, respectively. Direct plates (evaporation under heat lamp) from each of these solutions were made into "fixing" (approximately 7 μ g of silver nitrate)⁽²⁴⁾ and "nonfixing" (water) solutions on stainless steel planchets and counted. A second count was taken approximately three weeks later. The physical appearance of the plates was good, and accurate counting

Table III

EFFECT OF SOLUTION MEDIUM AND EXPOSURE TO AIR OF IODINE-131 PLANCHETTED SAMPLES

Number	Iodine-131 Solution Medium	Direct Plated		Net CPM		Δt days	$e^{-\lambda t}$		Percent Loss	Remarks		
		Vol.	Into	t_1	t_2		Exptl.	Calcd.				
1	0.01M HCl	25 λ	H ₂ O	7860	721	22.0	0.0917	0.1508	39.2 } Initial direct plates are nonreproducible; very large loss of iodide on exposure to air.			
2	"	"	"	6102	586	"	0.0960	"			36.4	
5	"	"	"	6700	651	"	0.0971	"			35.6	
6	"	"	"	8868	911	"	0.1027	"			31.9	
3	0.005M Na ₂ S ₂ O ₃	25 λ	H ₂ O	7025	781	22.0	0.1111	0.1508			26.3 } Same as above, but to a lesser extent than 0.01M HCl samples.	
4	"	"	"	6889	857	"	0.1244	"				
7	"	"	"	6430	780	"	0.1213	"	19.6			
8	"	"	"	6720	715	"	0.1063	"	29.5			
9	0.01M HCl	25 λ	0.1 ml AgNO ₃ (~7 μ g)	8617	1311	21.0	0.1521	0.1638	7.2 } Fair reproduction of direct plate; small loss of iodide on exposure to air.			
10	"	"	"	8296	1253	"	0.1510	"			7.8	
11	0.005M Na ₂ S ₂ O ₃	25 λ	0.1 ml AgNO ₃ (~7 μ g)	6579	1054	21.0	0.1602	0.1638	2.2 } Reproducible direct plates; little, if any, iodide loss on exposure to air.			
12	"	"	"	6530	1053	"	0.1612	"			1.6	

results could be obtained. It can be seen from Table III that reproducible direct plates cannot be obtained from either solution when they are plated into water media, due to the volatilization of varying amounts of iodine from the plate during the evaporation process. The effect is greater with those plates made from the hydrochloric acid solution than with those made from the sulfite solution. The iodine is also lost from the final plate during storage in air, probably due to the formation of elemental iodine or some other volatile oxidation product of iodine. The effect is again greater with those plates made from the acid solution. A somewhat similar study has been made by Anghileri who determined the extent of radioiodine losses from radiochromatograms exposed to air.⁽¹⁾

With respect to the direct plates into silver nitrate solution, the above volatilization losses are lessened considerably with the acid solution, and eliminated (or practically so) with the sulfite solution. For the preparation of direct plates of iodine-131 iodide solutions, therefore, it is recommended that the solutions be 0.005 M in sodium sulfite, and the direct plates be made into a solution containing a few micrograms of silver nitrate.

SUMMARY

A procedure has been developed for the determination of inorganic iodide in urine. The procedure yields a recovery of $87.2 \pm 1.5\%$ and has a detection limit of less than 50 dpm total iodine-131 in 1.5 liters of urine.

ACKNOWLEDGMENT

Appreciation is hereby expressed to J. Sedlet for his advice and constructive criticism during the course of this work.

APPENDIX A

DETAILED PROCEDURE*

1. Pipet 2.0 ml standardized potassium iodide solution (~ 10 mg I^- /ml) into a 600-ml beaker containing 300 ml of the urine sample (Note A).

(Note A: If 300 ml is not available, use the maximum possible volume - preferably not less than 100 ml.)
2. Add three drops octyl alcohol to the sample, and then acidify to a pH of 2-3 with 2 N sulfuric acid, using Hydrion paper as indicator.
3. Transfer the sample with 0.1 N sulfuric acid to the silver chloride column. Use a flow-rate of 25-30 ml per minute here and in subsequent columnar flows. Discard the effluent.
4. Wash the column with 200 ml 0.1 N sulfuric acid. Discard the effluent.
5. Add 100 ml chlorine solution (0.1 N in sulfuric acid) to the column. After approximately 20 ml (one column volume) of effluent (discard) has emerged from the column, stop the flow and allow the chlorine solution to set on the column for 5 minutes; then renew the flow, collecting the effluent in a 400-ml beaker.
6. Add 200 ml 0.1 N sulfuric acid to the column, and collect the effluent in the same beaker (Step 5) until Hydrion paper is no longer bleached by the effluent and becomes red. Discard the remainder of the effluent.
7. Neutralize the contents of the beaker with 6 M sodium hydroxide, using Hydrion paper as indicator. Add 5 ml excess. Bring contents to a boil. Cool to room temperature. Make acid with concentrated nitric acid, and transfer the contents to a 250-ml separatory funnel (Teflon stop-cock), using a minimum amount of distilled water as transfer agent.
8. Add 30 ml benzene and 5 ml 1 M hydroxylamine hydrochloride to the funnel. Shake for 30 seconds. Add 50 ml 1 M hydroxylamine hydrochloride, and shake again for 30 seconds. Add 3 ml 1 M sodium nitrite. Shake for 30 seconds. After separation of the layers, drain off and discard the colorless aqueous layer.
9. Add 30 ml carbon tetrachloride (Note B) to the violet organic layer, and then 15 ml distilled water containing 15 drops 1 M sodium bisulfite solution. Shake until the organic layer is colorless (Note C). After layer separation, drain off and discard the organic layer.

*Reagents, apparatus, and materials used in this procedure are listed in Appendices B and C.

(Note B: The carbon tetrachloride is added to increase the density of the organic phase to a point where it is heavier than the aqueous phase. This is done so that the phase containing the iodine may be retained in the funnel and not be subjected to transfer from one container to another.)

(Note C: If the organic phase does not become colorless, add the minimum amount of 1 M sodium bisulfite solution required to effect this change.)

10. Add 30 ml benzene to the funnel, and then 1 ml 6 N nitric acid and 1 ml 1 M sodium nitrite. Shake for 30 seconds. Add 1 ml 1 M sodium nitrite, and shake for 30 seconds. Add 5 ml 1 M hydroxylamine hydrochloride, and shake for 30 seconds. After layer separation, drain off and discard the colorless aqueous phase.
11. Add 15 ml distilled water, and shake for 15 seconds. After layer separation, discard the colorless aqueous layer.
12. Add 15 ml distilled water containing 15 drops 1 M sodium bisulfite. Shake until the upper layer becomes colorless (Note C above). After layer separation, collect the aqueous layer in a 100-ml beaker.
13. Add 1 ml 6 N nitric acid to the beaker and heat, with stirring, to the boiling point. Boil for 3 minutes (Note D). Stop heating and add, dropwise and with stirring, 2.0 ml 0.1 N silver nitrate to the hot solution. Heat the solution (Note E) to a gentle boil, and let it cool to room temperature.

(Note D: The boiling is necessary to remove the sulfur dioxide from solution.)

(Note E: This heating helps to coagulate the precipitate of silver iodide, making the subsequent filtering easier.)

14. After the solution has been cooled, filter the silver iodide onto a prepared weighed filter paper mounted in the two-piece filter funnel. (Note F). Wash the precipitate with three 5-ml portions of distilled water, and then with three 5-ml portions of absolute ethyl alcohol.

(Note F: The filter paper is prepared in the same manner as the precipitate is treated - i.e., washed, dried and weighed.)

15. After the precipitate is almost dry, remove the top part of the filter funnel. Carefully distribute the damp precipitate uniformly over the precipitate area of the filter paper with the flat tip of a stainless steel spatula (Note G).

(Note G: Upon drying, the silver iodide possesses a "flaky" appearance and does not uniformly cover the filter paper, resulting in many open areas on the filter paper. It is, therefore, necessary (for the accurate determination of the counting efficiency) to use the above precipitate distribution step.)

16. Dry the precipitate in an oven at 110°C for 10 minutes. Cool to room temperature in a desiccator and weigh (Note H).

(Note H: The precipitate should be weighed as soon as possible after cooling, as the photodecomposition of the silver iodide will, after a period of time, lead to a false silver iodide weight.)

17. Mount the weighed precipitate and filter paper on a two-inch stainless steel planchet, using double-coated tape and Mylar film. Beta and/or gamma count.
18. Calculate the iodine-131 content of the sample, as follows:

$$\text{Total dpm iodine-131/1500 ml urine}^* = \frac{(1500)(N_0)}{(V)(E)(Y)(0.8)},$$

where

V = sample urine volume, ml;

E = counting efficiency;

Y = chemical yield = mg AgI recovered/equivalent mg AgI added;

0.8 = minimum fraction of iodine in urine that is inorganically bound⁽¹²⁾;

N_0 = amount (cpm) iodine-131 present at time zero, t_0 ,
where $N_0 = N_t/e^{-\lambda t}$;

N_t = amount (cpm) iodine-131 present after time t;

t = $t_x - t_0$ (expressed in days) where t_x = time at which count was made, t_0 = approximate midpoint of sampling period;

$e^{-\lambda t}$ = calculated from time conversion and radioactive decay tables, using $T_{1/2} = 8.05$ days.

*This equation yields an approximate answer for the total dpm iodine-131 in 1500 ml of urine at sampling time. If the factor 0.8 is neglected, a more accurate answer is obtained for the dpm iodine-131 present as inorganic iodide in 1500 ml of urine.

APPENDIX B

REAGENTS

Reagents should be of analytical reagent grade, if possible.

Benzene - C_6H_6

Carbon tetrachloride - CCl_4

Chlorine solution - 0.1 N sulfuric acid saturated with chlorine gas from compressed gas cylinder

Ethyl alcohol, absolute - C_2H_5OH

Ferric alum indicator solution, approximately saturated - 40 g $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ /100 ml

Hydrion indicator paper (Micro Essential Laboratory, Brooklyn)

Hydroxylamine hydrochloride, 1 M - 6.95 g $NH_2OH \cdot HCl$ /100 ml

Nitric acid, 6 N - 97.5 ml concentrated HNO_3 /250 ml

Nitrobenzene - $C_6H_5NO_2$

Octyl alcohol - $C_8H_{17}OH$

Potassium iodide solution (~10 mg I^- /ml) - 6.54 g KI /500 ml. This solution must be standardized (see Appendix F)

Potassium thiocyanate solution, 0.1 N - 9.72 g $KSCN$ /liter. This solution must be standardized (see Appendix E)

Silver chloride - Fisher certified reagent (catalog No. S-174) $AgCl$ is sieved to obtain 20-40 mesh.

Silver nitrate solution, 0.1000 N - standard 0.1 N ampoule of $AgNO_3$ solution used.

Sodium bisulfite solution, 1 M - 5.2 g $NaHSO_3$ /50 ml

Sodium hydroxide solution, 6 N - 240 g $NaOH$ /liter

Sodium nitrite solution, 1 M - 3.45 g $NaNO_2$ /50 ml

Sulfuric acid, 0.1 N - 5.6 ml conc. H_2SO_4 /2000 ml

Sulfuric acid, 2 N - 28.1 ml conc. H_2SO_4 /500 ml

APPENDIX C

APPARATUS AND MATERIALS

Silver chloride column (see Appendix D)

Separatory funnel, 250 ml, with Teflon stopcock

Filter column, two-piece

Filter paper, Whatman No. 540, 2.1-cm diameter

APPENDIX D

PREPARATION OF SILVER CHLORIDE COLUMN

Fill the empty column with 0.1 N sulfuric acid. Leaving the stopcock open, add 20-40 mesh silver chloride to the column to a height of approximately 3 inches. Add 200 ml 0.1 N sulfuric acid to the column. If channeling appears to be present in the columnar contents - as shown by excessive flow-rate and bubble formation at the top surface of the silver chloride - then it will be necessary to backwash the column. Backwashing is accomplished by forcing 0.1 N sulfuric acid through the column from the bottom upwards, then allowing the displaced silver chloride to resettle into the bottom of the glass column. If, after this procedure, channeling or gassing is still apparent, light tapping on the bottom and sides of the column will normally complete the settling of the silver chloride. After the column has been so prepared, place a glass wool plug over the silver chloride, to prevent disturbance of the top layer of silver chloride during solution flow. The column is now ready for use.

When the column is not in use, a solution of 0.1 N sulfuric acid is kept on it. Due to the design of the outlet tube, the columnar liquid level will never be below the upper surface of the silver chloride, even if the stopcock is inadvertently left open.

APPENDIX E

POTASSIUM THIOCYANATE SOLUTION STANDARDIZATION⁽¹⁷⁾

Add 1 ml concentrated nitric acid to 25.0 ml water in a 100-ml beaker. To this, pipet 5.0 ml 0.1000 N silver nitrate. Add 1.0 ml ferric alum indicator solution. From a 10-ml micro-pipet, add the potassium thiocyanate solution dropwise to the beaker, using a magnetic stirrer for mixing. Titrate until a permanent reddish-brown color appears that does not fade after 5 minutes.

Note: The first perceptible color change to orange-red occurs at about 99% completion of the titration.

Calculation:

$$\text{Normality KSCN} = \frac{(\text{ml AgNO}_3)(\text{normality AgNO}_3)}{(\text{ml KSCN})}$$

APPENDIX F

POTASSIUM IODIDE SOLUTION STANDARDIZATION(17)

Pipet 2.0 ml potassium iodide solution ($\sim 10 \text{ mg I}^-/\text{ml}$) into a 100-ml beaker, containing 25.0 ml water. Add 1.0 ml concentrated nitric acid, and then pipet 5.0 ml 0.1000 N silver nitrate into the beaker. Add 3.0 ml nitrobenzene, using a magnetic stirrer for mixing. After the precipitate of silver iodide has agglomerated, leaving the solution relatively clear, add 1.0 ml ferric alum indicator solution. Titrate the excess silver nitrate with standard potassium thiocyanate solution until a permanent reddish-brown color appears that does not fade after 5 minutes.

Note: The first perceptible color change to orange-red occurs at about 99% completion of the titration.

Calculation:

$$\text{Iodide in potassium iodide solution, mg/ml} = \frac{126.91(AB - CD)}{E},$$

where

A = normality of the standard silver nitrate solution;

B = volume of silver nitrate taken, ml;

C = normality of standard potassium thiocyanate solution;

D = volume of potassium thiocyanate required by the excess silver nitrate, ml;

E = potassium iodide solution volume, ml;

126.91 = atomic (equivalent) weight of iodine.

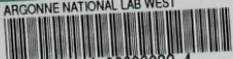
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