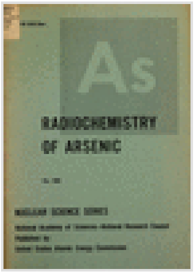

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RADIOCHEMISTRY OF ARSENIC

HAROLD C. BEARD

Florida State University,
Tallahassee, Florida, January 1960

revised by

J. G. CUNINGHAME

Atomic Energy Research Establishment,
Harwell, Didcot, Berkshire, England, January 1965

Issued: November 1965

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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FOREWORD

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences - National Research Council. Its members represent government, industrial, and university laboratories in the areas of radiochemistry and nuclear chemistry. Support for the activities of this and other subcommittees of the Committee on Nuclear Science is provided by a grant from the National Science Foundation.

The subcommittee has concerned itself with preparation of publications, encouraging and supporting activities in nuclear education, sponsoring symposia on selected current topics in radiochemistry and nuclear chemistry, and investigating special problems as they arise. A series of monographs on the radiochemistry of essentially all the elements and on radiochemical techniques is being published. Initiation and encouragement of publication of articles on nuclear education in various subject areas of chemistry have occurred, and development and improvement of certain education activities (e.g., laboratory and demonstration experiments with radioactivity) have been encouraged and assisted. Radioactive contamination of reagents and materials has been investigated and specific recommendations made.

This series of monographs has resulted from the need for comprehensive compilations of radiochemical and nuclear chemical information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or with a specialized technique. The U. S. Atomic Energy Commission has sponsored the printing of the series.

Comments and suggestions for further publications and activities of value to persons working with radioactivity are welcomed by the Subcommittee.

N. E. Ballou, Chairman
Subcommittee on Radiochemistry

Preface to the revised edition

A considerable number of papers have appeared in the literature on the radiochemistry and chemistry of arsenic since the first edition of the monograph was published. The general form and much of the original content of the monograph has been retained, substantial additions being made where necessary.

The reviser would like to thank Mr. R. W. Clarke, Information Officer of the Chemistry Division, A.E.R.E., for his great help in conducting a very thorough literature search.

RADIOCHEMISTRY OF ARSENIC

HAROLD C. BEARD

Florida State University,
Tallahassee, Florida, January 1960

revised by

J. G. CUNINGHAME

Atomic Energy Research Establishment
Harwell, Didcot, Berkshire, England, January 1965

I. A SELECTION OF GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF ARSENIC

Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Volume 9, Chapter 51, pp. 1-338, Longmans, Green and Co., Inc., New York, 1947.

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Sneed, M. C. and Brasted, R. C., "Comprehensive Inorganic Chemistry," Volume 5, Introduction pp. 3-10, Chapter 2, pp. 106-152, D. Van Nostrand Co., Princeton, N.J., 1956.

Remy, H. "Treatise on Inorganic Chemistry" Elsevier Amsterdam, 1956.

Jacobsen, C. A., "Encyclopedia of Chemical Reactions," pp. 264-500, Reinhold Publishing Co., 1946.

McAlpine, R. K., and Soule, B. A., "Qualitative Chemical Analysis," 4th Edition D. Van Nostrand Co., Inc., New York, 1956.

Holness, H., "Advanced Inorganic Qualitative Analysis," pp. 75-79 and pp. 152-153, Pitman and Sons, London, 1957.

Willard, H. H. and Diehl, H., "Advanced Quantitative Analysis," pp. 339-345, D. Van Nostrand Co., New York, 1943.

Walton, H. F., "Principles and Methods of Chemical Analysis," pp. 161-163 and pp. 411-412, Prentice-Hall, Inc., New York, 1952.

Hillebrand, W. F., Lundell, G. E. F., Bright, H. A. and Hoffman, J. I., "Applied Inorganic Analysis," Chapter 13, pp. 256-272, 2nd Edition, John Wiley and Sons, New York, 1953.

Charlot, G. and Bejier, D. translated by Murray, R. C., "Quantitative Inorganic Analysis," pp. 335-342, Methuen and Co., London; John Wiley and Sons, Inc., New York, 1957.

Furman, N. H., "Standard Methods of Chemical Analysis" 6th Edition. Vol. 1 pp. 106-107. Van Nostrand, New York, 1962.

II. GENERAL REVIEWS OF THE RADIOCHEMISTRY OF ARSENIC

Smales, A. A., "Neutron Activation Analysis," Chapter 19, pp. 518-545 in Yoe, J. H. and Koch, J. J., Jr., "Trace Analysis," John Wiley and Sons, New York, 1957.

III. SUMMARY OF STATISTICAL PHYSICAL PROPERTIES OF ARSENIC(1)

Outer electronic configuration $4s^2\ 4p^3$
Molecular state of gas $As_4 \rightleftharpoons As_2$
Atomic volume, 13.13 ml. (metal)
Melting point, 814.5°C. (36 atm).
Boiling point, sublimes at 610°C.
Density, 5.7 g/cc (metal); 3.9 g/cc (yellow)
Radius, covalent, 1.21 Å
Radius, crystal, As^{-3} 2.22 Å ; As^{+3} 0.69Å ; As^{+5} (AsO_3^-) 0.47 Å
Ionization potential, ~ 10 e.v.
Electronegativity, 2.0 on the Pauling scale.
Principal oxidation states, -3, +3, +5
E^o, $As + 3\ H_2O \rightleftharpoons H_3AsO_3 + 3\ H^+ + 3\ e^-$, -0.25 v. ($HAsO_2$); $AsO_2 + 2\ H_2O \rightleftharpoons H_3AsO_4 + 2\ H^+ + 2\ e^-$, -0.559 v.
Heat capacity, 0.082 cal/gram.

IV TABLE OF ISOTOPES

Isotope	Half life	Some methods of preparation	Principal types of decay	Energy of principal β-radiations MeV	Energy of principal γ-radiations, MeV (with percentage of total γ's where shown)
As^{68}	7m	Ge^{70}(p, 3n)	β^+		
As^{69}	15m	Ge^{70}(p, 2n)	E.C. (~3%)		
			β^+ (~97%)	2.9	
As^{70}	52m	Ge^{70}(d, 2n)	E.C. (3%)		
		d. Se^{70}	β^+ (10%)	1.44	
			E.C. (5.3%)		
			β^+ (74.7%)	2.144	
			E.C. (0.18%)		
			β^+ (6.1%)	2.89	
			γ		1.04
As^{71}	62h	Ge^{70}(d,n)	β^+ (3%)	0.25	
		d. Se^{71}	β^+ (6%)	0.79	
			E.C. (58%)		
			β^+ (33%)	0.813	
			γ		0.175
As^{72}	26h	Ga^{69}(α, n)	E.C. (21.2%)		
		Ge^{72}(p, n)	β^+ (3.6%)		
		Ge^{72}(d, 2n)	β^+ (56.2%)	2.50	
		d. Se^{72}	β^+ (19%)	3.34	
			γ		0.630 (8)
			γ		0.835 (75)
As^{73}	76d	Ge^{72}(d, n)	E.C.		
		d. Se^{73}	γ		0.0135($e/\gamma > 1300$) 0.054($e/\gamma \sim 5$) [N.B. These γ's are from decay of Ge^{73m}, $t_{1/2}$ 0.33S].
As^{74}	17.5d	Ga^{71}(α, n)	E.C. ($\leqslant$ 1%)		
		Ge^{74}(d, 2n)	β^+ ($\leqslant$ 0.1%)		
		Ge^{74}(p, n)	E.C. (38%)		
		As^{75}(n, 2n)	β^+ (25%)	0.92	
			E.C. (2.2%)		
			β^+ (2.8%)	1.53	
			β^- (16%)	0.69	
			β^- (16%)	1.36	
			γ		0.596 (80)
			γ		0.635(20)
As^{75}	100% natural abundance				
As^{76}	26.5h	As^{75}(n, γ)	β^- (5.1%)		
		As^{75}(d, p)	β^- (6.9%)	1.748	
		Br^{79} (n, α)	β^- (35%)	2.405	
		Se^{76} (n, p)	β^- (53%)	2.965	
			γ		0.559 (71)
			γ		0.658 (6)
			γ		1.127 (16)
As^{77}	39h	Ge^{76} (d, n)	β^- (2.5%)		
		fission	β^- (97.5%)	0.69	
		d. Ge^{77}			
			γ (weak)		0.086 (4)
			γ (weak)		0.160 (7)
			γ (weak)		0.246 (67)
			γ (weak)		0.524 (22)

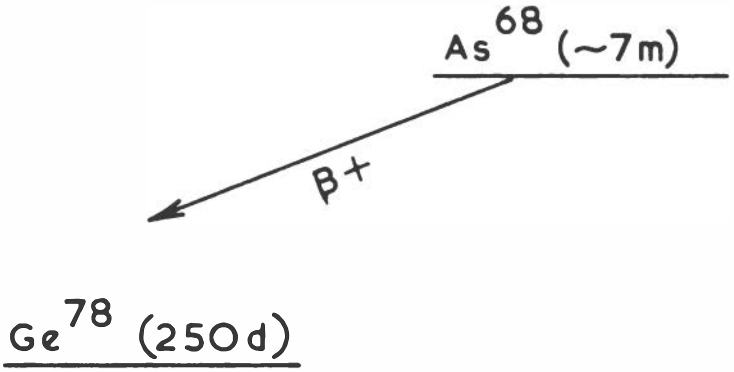
Isotope	Half life	Some methods of preparation	Principal types of decay	Energy of principal β-radiations MeV	Energy of principal γ-radiations MeV (with percentage of total γ's where shown)
As^{78}	91m	$Br^{81}(n, \alpha)$	β^- (30%)	1.4	
		$Se^{78}(n, p)$	β^- (70%)	4.1	
		fission d.			
		Ge^{78}	γ		0.270
			γ		0.610
			γ		0.800
			γ		1.280
			γ		2.680
As^{79}	9m	$Se^{80}(\gamma, p)$	β^- (5%)		
		$Se^{80}(n,pn)$	β^- (95%)	2.15	
		$Se^{82}(d, \alpha n)$			
As^{80}	15.35	$Se^{80}(n, p)$	β^- (0.8%)		
			β^- (4.3%)	3.7	
			β^- (3.5%)	4.1	
			β^- (1.7%)	4.2	
			β^- (1.4%)	4.5	
			β^- (32%)	5.4	
			β^- (56%)	6.0	
			γ		0.66
As^{81}	31s	$Se^{82}(\gamma, p)$	β^- (100%)	3.8	

For further information on the radiations of the arsenic isotopes see:-

B. S. Dzhelepov and L. K. Peker "Decay Schemes of radioactive isotopes", Pergamon Press, Oxford, 1961.
D. Strominger, J. M. Hollander and G. T. Seaborg, Revs. Mod. Phys. 30.2 Part II 1958.
1960 Nuclear Data Tables NAS-NRC Washington 1960.
1959 Nuclear Data Tables NAS-NRC Washington 1959.
Nuclear Level Schemes A = 40 to A = 92 NAS-NRC Washington 1955.

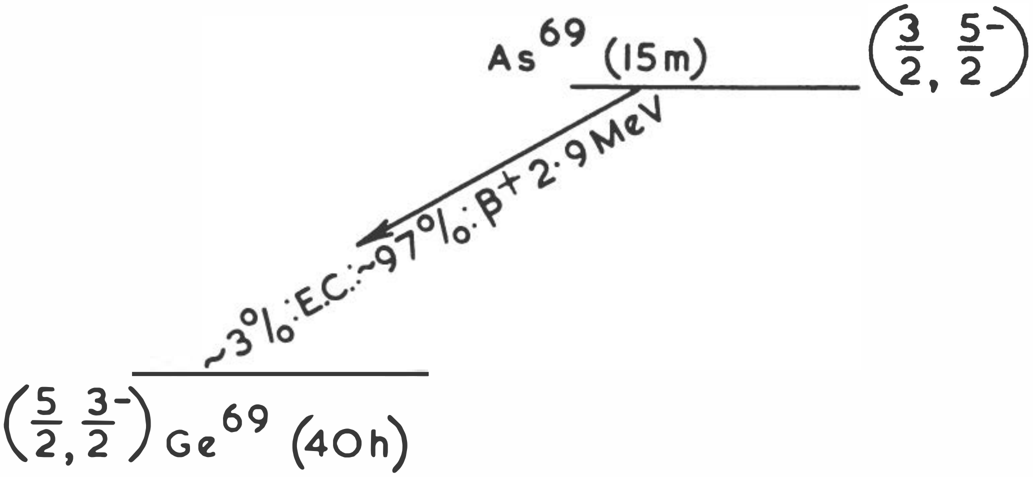
V DECAY SCHEMES

As^{68}



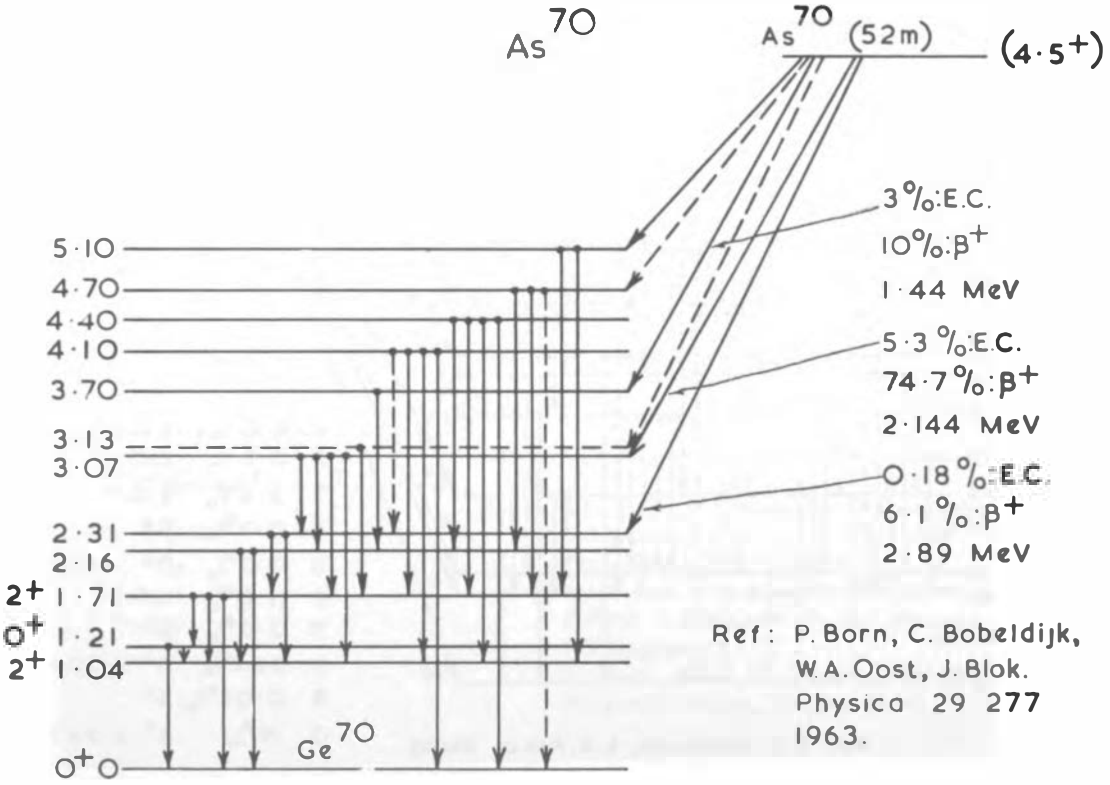
Ref : F. D. S. Butement, E. G. Prout.
Phil. Mag. 46. 357. 1955.

As^{69}



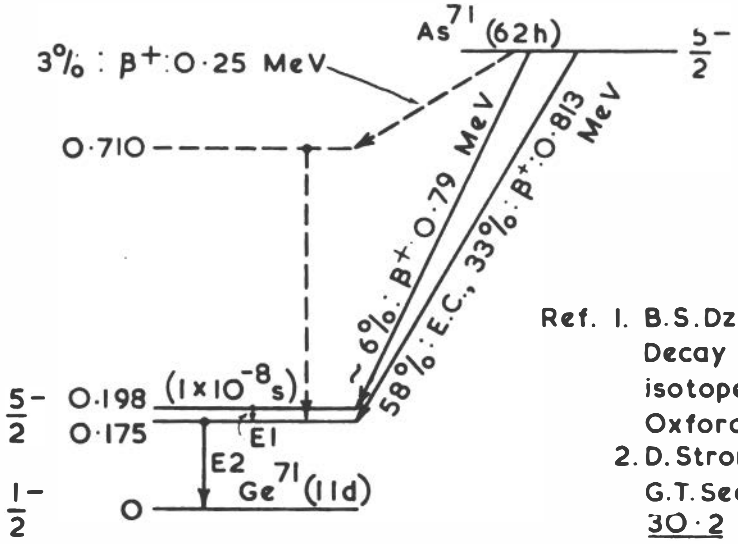
Ref : F. D. S. Butement, E. G. Prout.
Phil. Mag. 46. 357. 1955.

As^{70}



Ref: P. Born, C. Bobeldijk, W. A. Oost, J. Blok. Physica 29 277 1963.

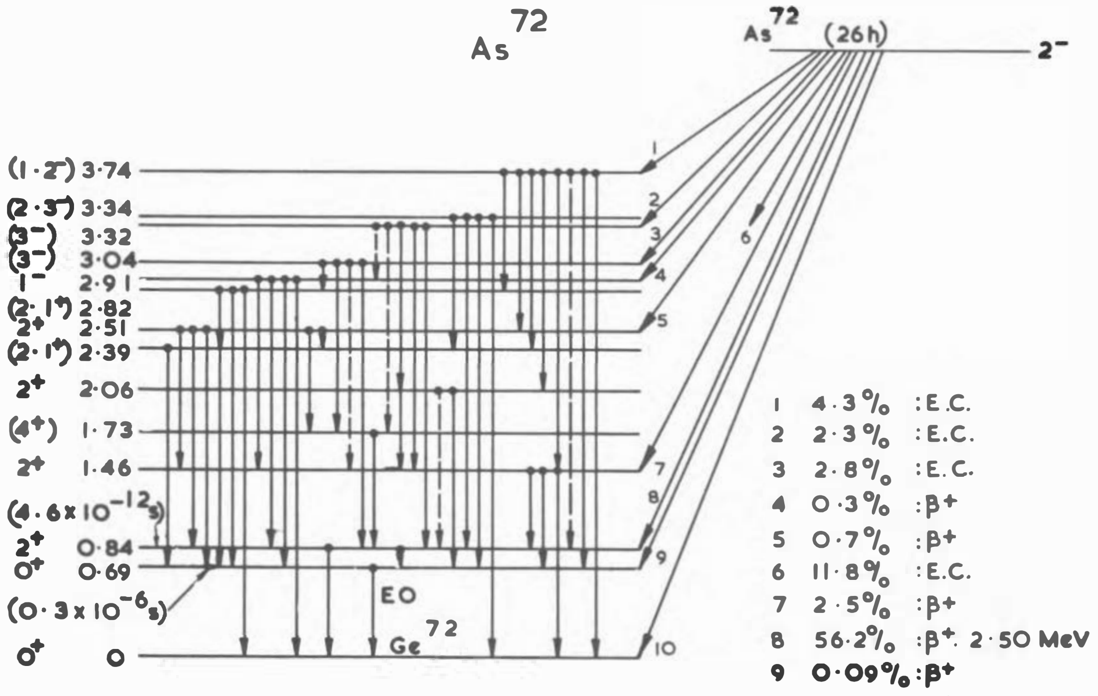
As^{71}



Ref. 1. B.S. Dzhelepov, L.K. Peker. Decay schemes of radioactive isotopes. Pergamon Press, Oxford. 1961.

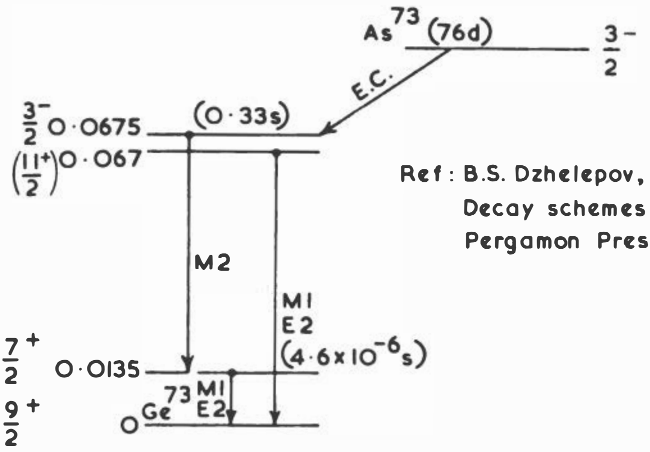
2. D. Strominger, J.M. Hollander, G.T. Seaborg Revs. Mod. Phys. 30·2 Pt. II 1958.

As^{72}



Ref. B.S. Dzhelepov, L.K. Peker. Decay schemes of radioactive isotopes. Pergamon Press, Oxford 1961.

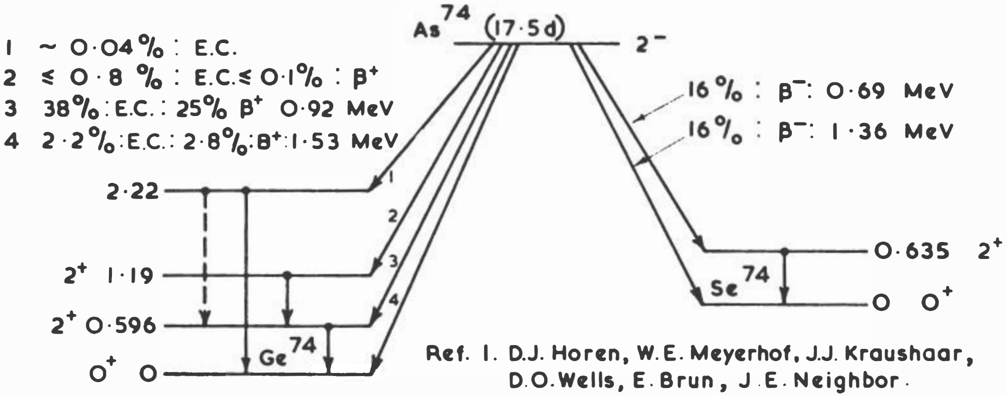
As^{73}



Ref: B.S. Dzhelepov, L.K. Peker.
Decay schemes of radioactive isotopes
Pergamon Press, Oxford 1961.

As^{74}

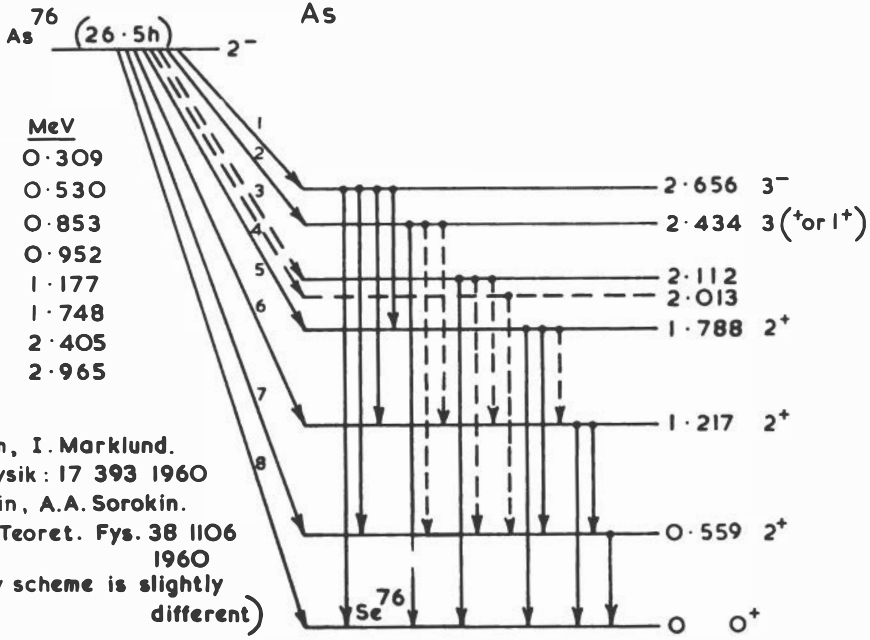
1 ~ 0·04 % : E.C.
2 ≤ 0·8 % : E.C. ≤ 0·1 % : β^+
3 38 % : E.C. : 25 % β^+ 0·92 MeV
4 2·2 % : E.C. : 2·8 % : β^+ : 1·53 MeV



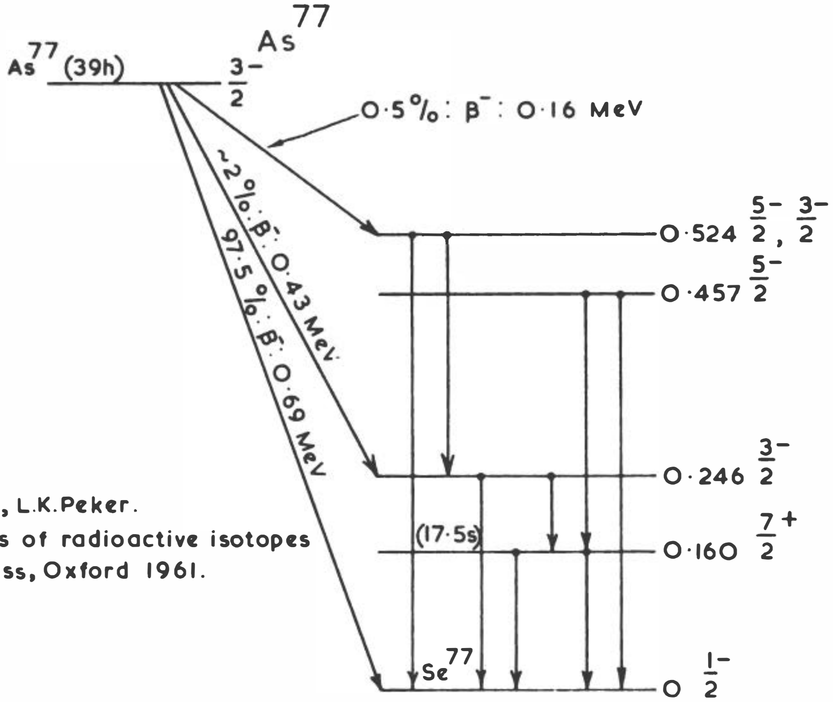
Ref. 1. D.J. Horen, W.E. Meyerhof, J.J. Kraushaar, D.O. Wells, E. Brun, J.E. Neighbor. Phys. Rev. 113 875 1959.
2. T. Yamazaki, H. Ikegami, M. Sakai. J. Phys. Soc. Japan 15 957 1960
3. B.S. Dzhelepov. Isobaric nuclei of mass number 74 Pergamon Press, Oxford 1963.

As^{76}

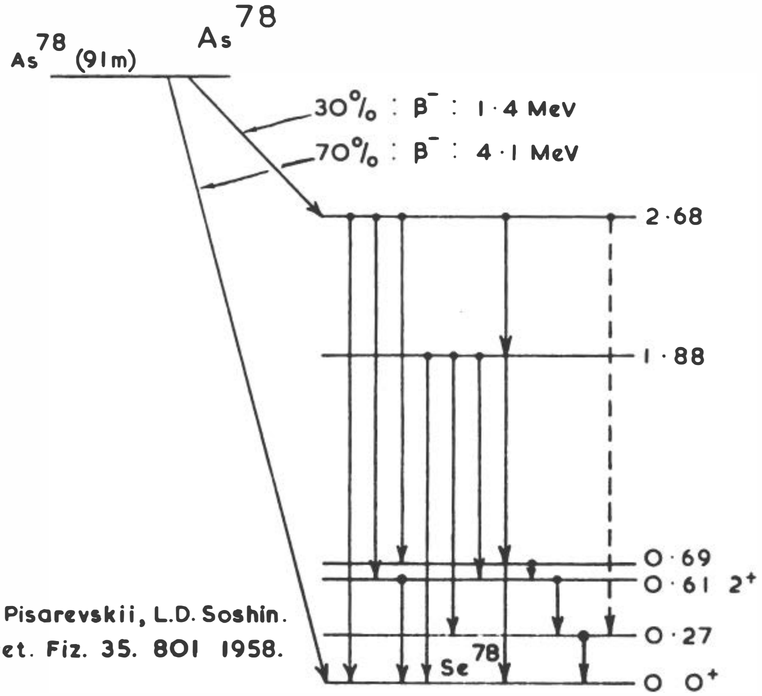
β^-	%	MeV
1	1·2	0·309
2	1·0	0·530
3	0·6	0·853
4	0·2	0·952
5	2·1	1·177
6	6·9	1·748
7	35	2·405
8	53	2·965



Ref. 1. G. Bäckstrom, I. Marklund. Arkiv. för Fysik: 17 393 1960
2. N.N. Delyagin, A.A. Sorokin. Zhur. Eks i Teoret. Fys. 38 1106 1960
(whose decay scheme is slightly different)

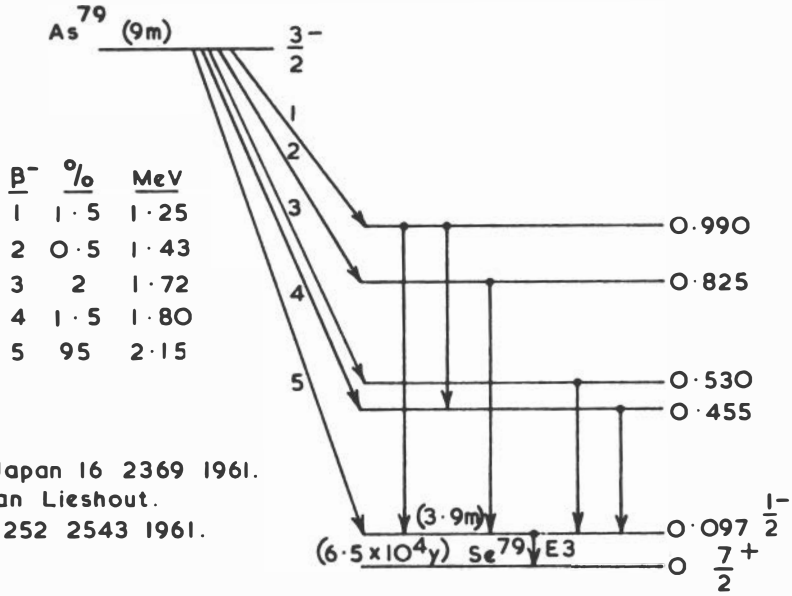


Ref: B.S. Dzhelepov, L.K. Peker.
Decay schemes of radioactive isotopes
Pergamon Press, Oxford 1961.



Ref. Iu. A. Nemilov, A.N. Pisarevskii, L.D. Soshin.
Zhur. Exsp. i. Teoret. Fiz. 35. 801 1958.

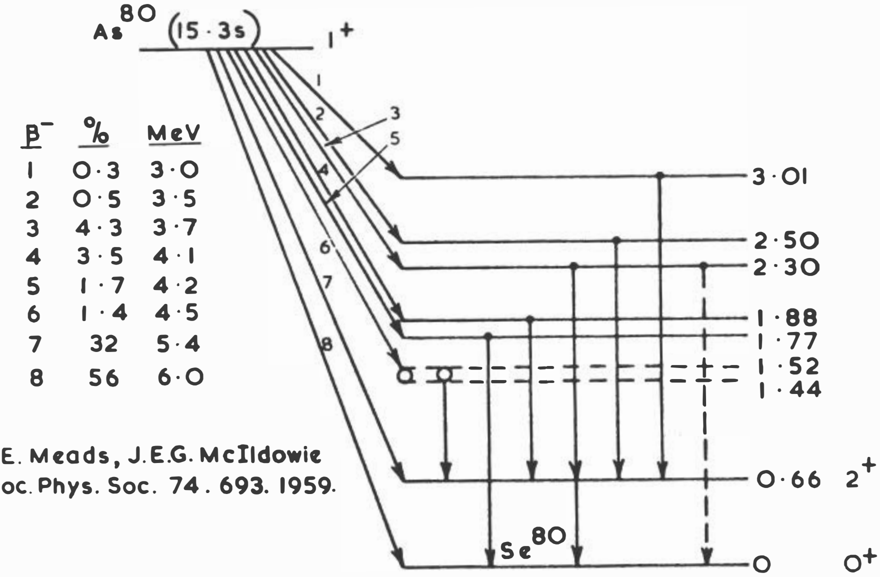
As^{79}



β^-	%	MeV
1	1·5	1·25
2	0·5	1·43
3	2	1·72
4	1·5	1·80
5	95	2·15

Ref. 1. T. Kuryoanagi
J. Phys. Soc. Japan 16 2369 1961.
2. C. Ythier, R. van Lieshout.
Compt. rendus 252 2543 1961.

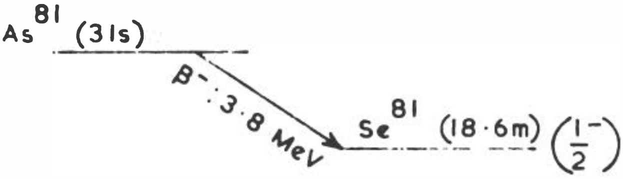
As^{80}



β^-	%	MeV
1	0·3	3·0
2	0·5	3·5
3	4·3	3·7
4	3·5	4·1
5	1·7	4·2
6	1·4	4·5
7	32	5·4
8	56	6·0

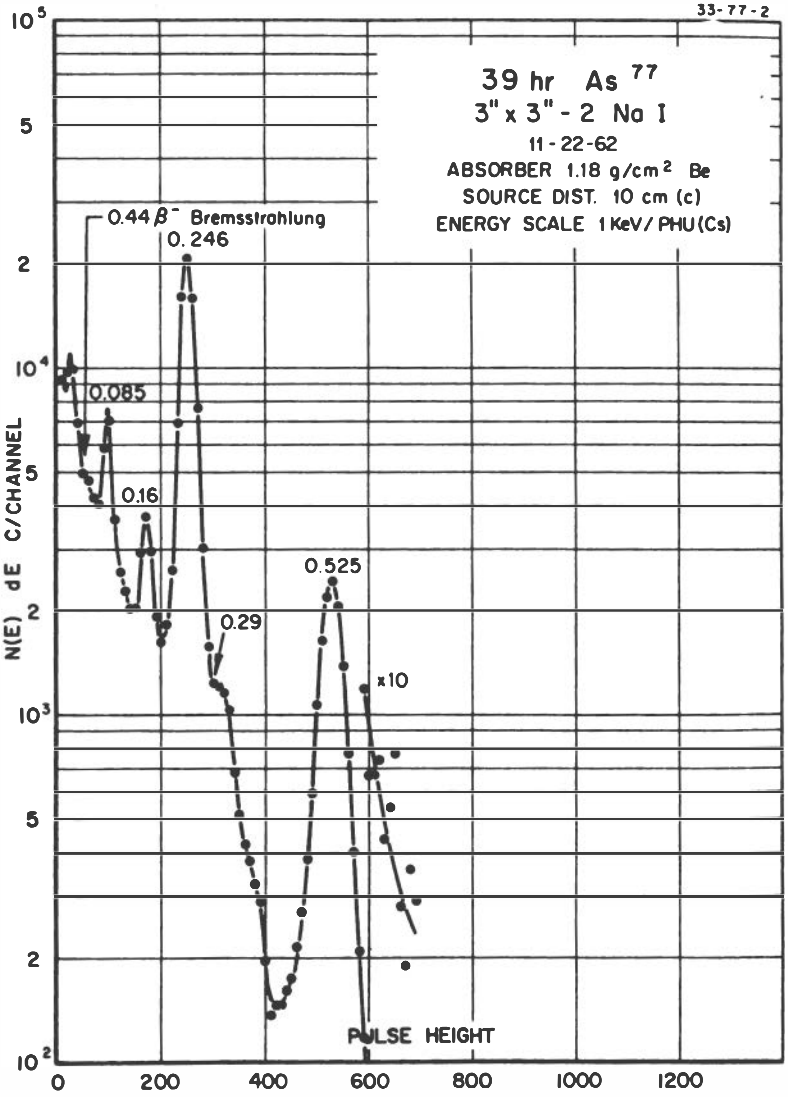
Ref: R.E. Meads, J.E.G. McIldowie
Proc. Phys. Soc. 74. 693. 1959.

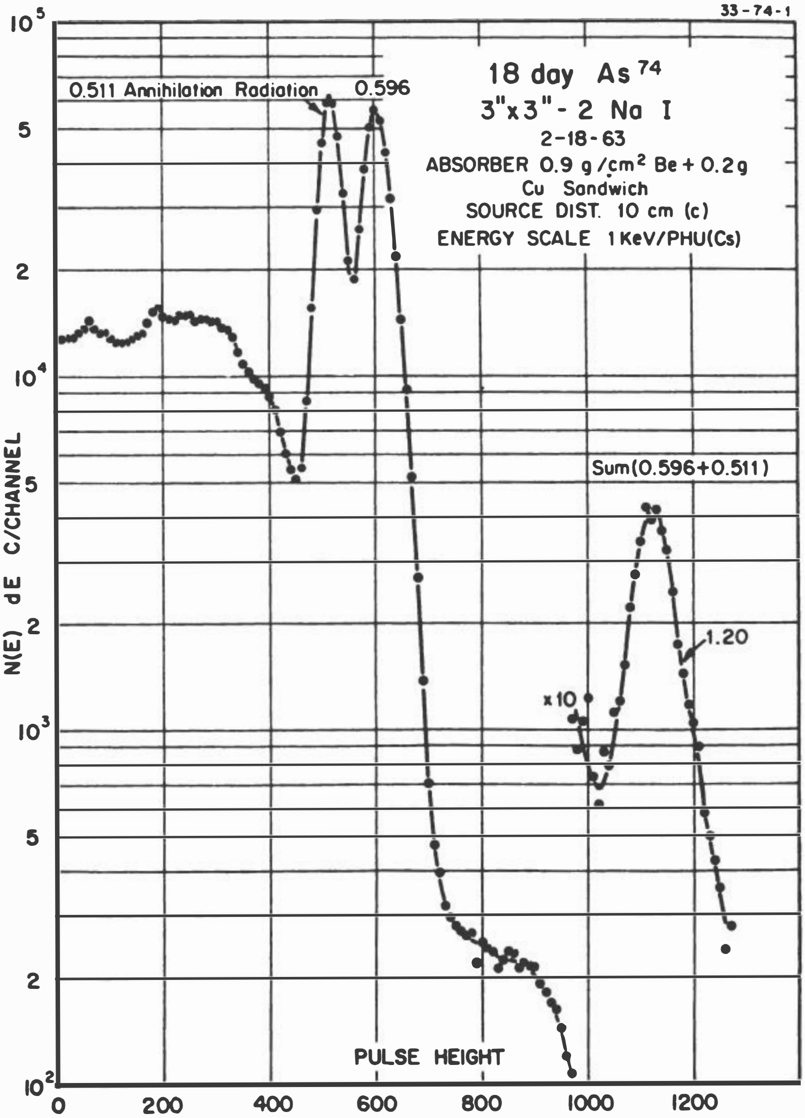
As^{81}

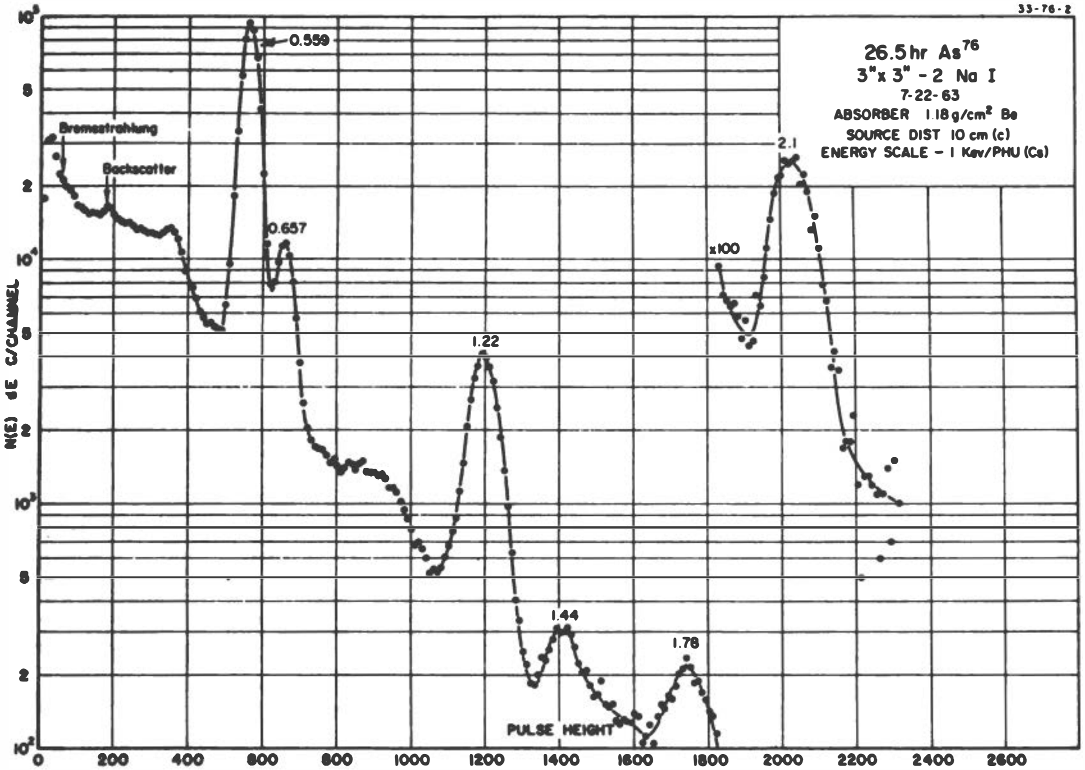


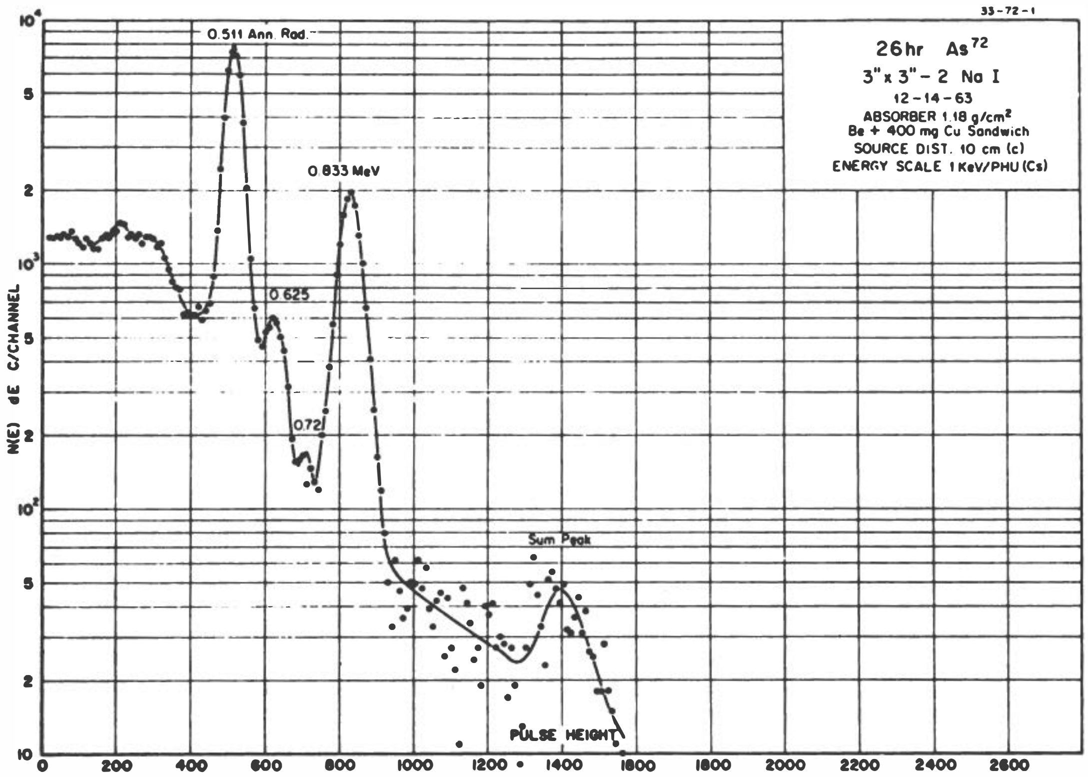
Ref: H. Morinaga, T. Kuroyanagi,
H. Mitsui, K. Shoda.
J. Phys. Soc. Japan. 15 213 1960.

VI γ SPECTRA

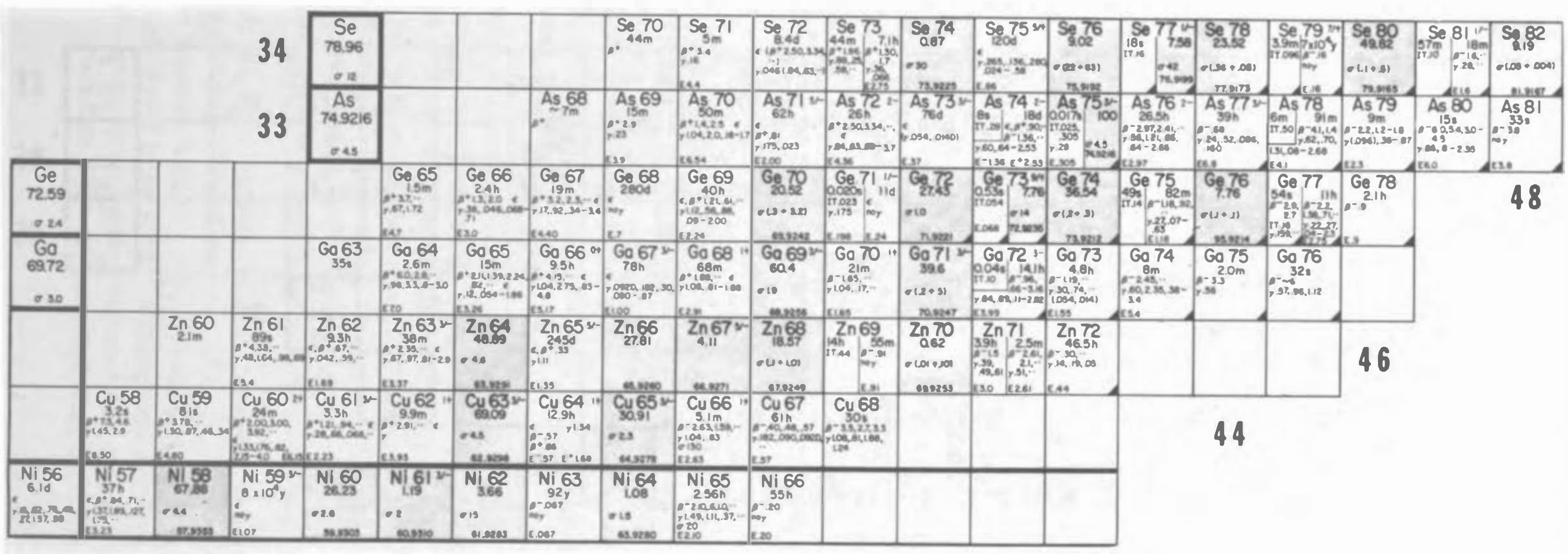


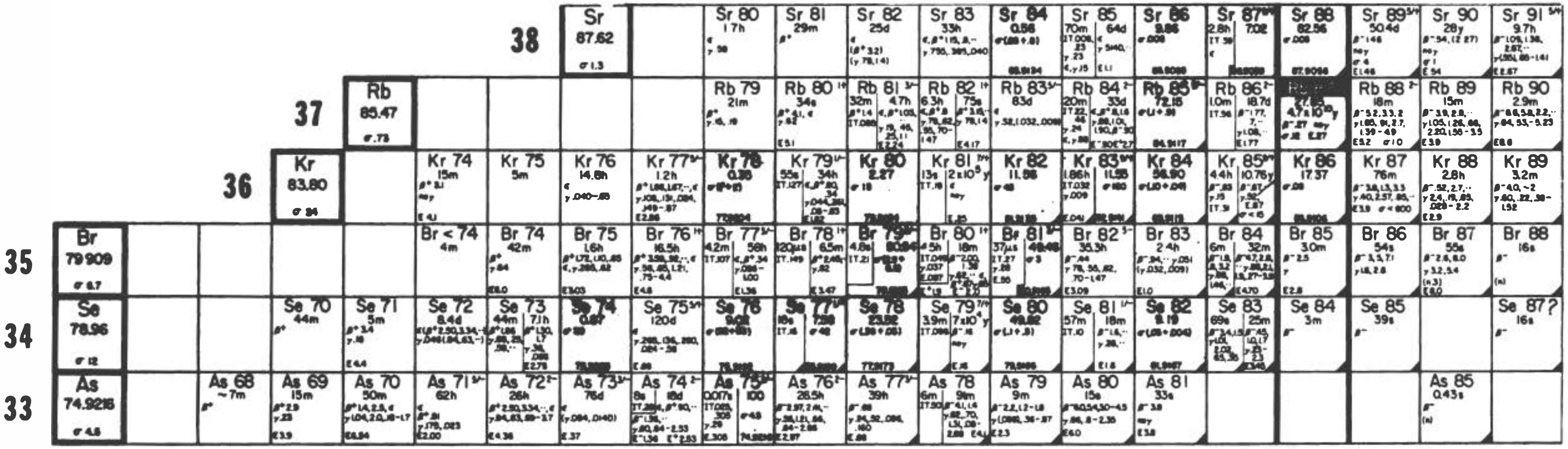

33-74-1
18 day As^{74}
3"x3" - 2 Na I
2-18-63
ABSORBER 0.9 g/cm^2 Be + 0.2g
Cu Sandwich
SOURCE DIST. 10 cm (c)
ENERGY SCALE 1 KeV/PHU(Cs)
0.511 Annihilation Radiation
0.596
Sum(0.596+0.511)
1.20
x10
N(E) dE C/CHANNEL
PULSE HEIGHT
10^5
5
2
10^4
5
2
10^3
5
2
10^2
0
200
400
600
800
1000
1200


33-76-2
26.5 hr As76
3"x 3" - 2 Na I
7-22-63
ABSORBER 1.18 g/cm² Be
SOURCE DIST 10 cm (c)
ENERGY SCALE - 1 Kev/PHU (Cs)
0.559
0.657
1.22
1.44
1.78
2.1
x100
Bremsstrahlung
Backscatter
N(E) dE C/CHANNEL
PULSE HEIGHT
10⁵
5
2
10⁴
5
2
10³
5
2
10²
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
2600


33-72-1
26hr As^{72}
3"x 3" - 2 Na I
12-14-63
ABSORBER 1.18 g/cm^2
Be + 400 mg Cu Sandwich
SOURCE DIST. 10 cm (c)
ENERGY SCALE 1 KeV/PHU (Cs)
0.511 Ann. Rad.
0.833 MeV
0.625
0.72
Sum Peak
PULSE HEIGHT
N(E) dE C/CHANNEL
10^4
5
2
10^3
5
2
10^2
5
2
10
0
200
400
600
800
1000
1200
1400
1800
1800
2000
2200
2400
2600

VII RELEVANT PORTION OF CHART OF THE NUCLIDES




38
Sr 87.62 σ 1.3
Sr 80 1.7h
Sr 81 29m
Sr 82 25d
Sr 83 33h
Sr 84 0.56
Sr 85 70m 64d
Sr 86 9.86
Sr 87 2.8h 7.02
Sr 88 82.56
Sr 89 50.4d
Sr 90 28y
Sr 91 9.7h
37
Rb 85.47 σ.73
Rb 79 21m
Rb 80 34s
Rb 81 32m 4.7h
Rb 82 6.3h 75s
Rb 83 83d
Rb 84 20m 33d
Rb 85 72.15
Rb 86 1.0m 18.7d
Rb 87 27.85 4.7×10¹⁰y
Rb 88 18m
Rb 89 15m
Rb 90 2.9m
36
Kr 83.80 σ 24
Kr 74 15m
Kr 75 5m
Kr 76 14.8h
Kr 77 1.2h
Kr 78 0.35
Kr 79 55s 34h
Kr 80 2.27
Kr 81 13s 2×10⁵y
Kr 82 11.56
Kr 83 1.86h 11.55
Kr 84 56.90
Kr 85 4.4h 10.76y
Kr 86 17.37
Kr 87 76m
Kr 88 2.8h
Kr 89 3.2m
35
Br 79.909 σ 6.7
Br < 74 4m
Br 74 42m
Br 75 1.6h
Br 76 16.5h
Br 77 4.2m 56h
Br 78 6.5m
Br 79 4.8s 50.54
Br 80 4.5h 18m
Br 81 37μs 49.46
Br 82 35.3h
Br 83 2.4h
Br 84 6m 32m
Br 85 3.0m
Br 86 54s
Br 87 55s
Br 88 16s
34
Se 78.96 σ 12
Se 70 44m
Se 71 5m
Se 72 8.4d
Se 73 44m 7.1h
Se 74 0.87
Se 75 120d
Se 76 9.02
Se 77 18s 7.58
Se 78 23.52
Se 79 3.9m 7×10⁴y
Se 80 49.82
Se 81 57m 18m
Se 82 9.19
Se 83 69s 25m
Se 84 3m
Se 85 39s
Se 87? 16s
33
As 74.9216 σ 4.5
As 68 ~7m
As 69 15m
As 70 50m
As 71 62h
As 72 26h
As 73 76d
As 74 8s 18d
As 75 0.017s 100
As 76 26.5h
As 77 39h
As 78 6m 9m
As 79 9m
As 80 15s
As 81 33s
As 85 0.43s

VIII. REVIEW OF THE CHEMISTRY OF ARSENIC OF INTEREST TO RADIOCHEMISTS

1. General properties

Arsenic as the element, exists in two distinct crystalline modifications, the grey or metallic stable form and the yellow form.(1) The grey metallic form is an excellent conductor of heat, but a poor conductor of electricity. At atmospheric pressure, it sublimes at 610°C, at 400°C it burns with a white flame forming the sesquioxide, As_4O_6. It takes fire in chlorine and combines, when heated, with most metals to form arsenide. It reacts readily with sulfur when heated. It is unaffected by hydrochloric acid in the absence of oxygen, but it oxidized by warm, dilute or concentrated nitric acid.

Yellow arsenic is obtained when arsenic vapour is chilled rapidly. It is extremely volatile and is more reactive than metallic arsenic and phosphoresces at room temperature. It is metastable and passes rapidly into the metallic form. A form of arsenic called black arsenic is apparently amorphous and has properties between those of the other two forms. It is obtained by the thermal decomposition of arsine as in the Marsh test.

The valency states of arsenic are +5, +3 and -3. Exchange between the +3 and +5 states in solution is slow, and it is advisable to carry out some reduction/oxidation cycle when adding carrier to trace arsenic. Such a cycle is often automatically incorporated, as when arsenic is oxidised to As(V) while germanium is distilled, and is then reduced to As(III) for its own distillation. If the proposed procedure does not include steps such as these, a convenient method is oxidation by potassium bromate followed by reduction with potassium metabisulfite.

Arsenic trihalides are prepared by the direct union of the elements or the action of the oxide or sulfide with halogen. (1) The compounds are covalent and soluble in non-polar solvents such as benzene and CS_2. $AsCl_3$ is easily hydrolyzed except in highly acid solution. Arsenic forms no pentahalide other than the gaseous fluoride, AsF_5. Arsenic can be reduced from the halide in a hot solution by hypophosphite, sulfurous acid, chromous chloride or cuprous chloride.

Another very important arsenic compound is the gaseous hydride AsH_3, known as arsine. This may be formed by hydrolysis of an arsenide, reduction from higher oxidation states by Zn or Sn in acid solution, or by electrolysis using a mercury or lead cathode. Arsine is decomposed in the well-known Marsh test by heating in a small glass tube, with the resulting deposition of a black arsenic metal "mirror" on the walls of the tube. Another familiar test, the Gutzeit method, utilises the reaction of arsine with a test paper impregnated with mercuric chloride or bromide, which gives a brown coloration.

Arsenic sesquioxide As_4O_6 is obtained when the element or the sulfide is roasted in air. It has a solubility of 2.04g/100g of water at 25°C.(1) That it readily dissolves in alkali solutions to form arsenite indicates acidic properties. The ionisation constant of arsenious acid has been calculated to be $6x10^{10}$ although the acid has never been isolated as such. The formulae of various arsenites are different and often quite complex. The oxide in alkaline solution is used as a primary standard reducing agent in oxidation - reduction titrimetry.

Arsenic(V) oxide is a white, amorphous, fusible powder prepared by the dehydration of arsenic acid. Ortho-arsenic acid, H_3AsO_4, is obtained when elementary arsenic or As_4O_6 is oxidised with concentrated nitric acid or chlorine water. The anhydrous acid, when heated, readily loses water to form the oxide, As_4O_{10}.

Arsenic(V) acid ($K = 5.0 \times 10^{-3}$) is weaker than phosphoric acid and arsenate salts hydrolyse more than the phosphate salts (1). Primary, secondary, and tertiary orthoarsenates are known, as well as meta- and pyroarsenate. They strongly resemble the corresponding phosphates in solubility and crystal form, many phosphate-arsenate pairs being isomorphous. Only the alkali-metal tertiary orthoarsenates are soluble in water so quantitative precipitation is possible with the silver ion, magnesia mixture, and with ammonium molybdate in nitric acid. These reactions are analogous to the phosphate, and that element will be coprecipitated. Contamination by tin, antimony and probably germanium may be avoided by complexing these elements with citrate or tartrate (2). The arsenate ion may be determined by an indirect process based on the precipitation of $MgNH_4AsO_4$, and the subsequent titration with EDTA of the magnesium contained in the precipitate (3).

The insolubility of the sulfides of arsenic in hydrochloric acid is frequently used to separate arsenic from other elements. The trisulfide As_2S_3, is a bright yellow compound readily obtained in a colloidal state if precipitation is carried out in solutions of low ionic strength, as when a solution of arsenious acid is saturated with H_2S. (1) Arsenic of either valency can be separated from elements other than those of the hydrogen sulfide group by precipitation in acid solution, and from elements of the copper group by precipitation in alkaline solution. (3) The precipitation of As_2S_5 in a strongly acid solution of an arsenate with H_2S is slow, and the product is usually a mixture of As_2S_5 and As_2S_3 because of the reducing property of H_2S. (1) If the arsenic is present as As(V) initially, it is advantageous to catalyse its reduction to As(III) by a little iodide. Precipitation of trivalent arsenic away from quadrivalent tin and germanium is possible in a hydrochloric-hydrofluoric acid solution by complexing the elements other than arsenic.

As_2S_3 can be dissolved by concentrated nitric acid, concentrated sulfuric acid or ammonia and hydrogen peroxide. (2) Sulfides, like their oxygen analogues, have acidic properties and dissolve readily in strong bases. (1) The sulfide dissolves readily in solutions of sulfide ion, the sulfide ions in solution acting as a base. These thio-ions are quite stable in neutral or alkaline solutions, but acidification results in reprecipitation of the sulfide and liberation of H_2S. Thus, the sulfides of arsenic are amphoteric.(1)

The usual macro methods for the determination of arsenic are (1) by weighing as the trisulfide; (2) by precipatation as silver arsenate of which the silver content is then determined by Volhard's method; and (3) by iodimetric titration of the trivalent compound.(4)

2. Separation methods

(a) Halide distillation (See also NAS-NS 3108, p. 13)

As(III) may be quantitatively distilled as chloride or bromide from concentrated HCl or HBr solutions. The distillation must be carried out in the presence of a reductant, since the only pentahalide of arsenic is the gaseous AsF_5. Cuprous chloride, ferrous sulphate, sulfurous, hydriodic or hydrobromic acids are suitable reductants.

Nitrate, $GeCl_4$ (b.p. 86°C) and $SnCl_4$ (b.p. 115°C) interfere. Nitrates can be eliminated by fuming with sulfuric acid, care being taken not to volatilise the arsenic, while $SnCl_4$ can be complexed by adding phosphoric acid. If germanium is present it is advisable to eliminate it before distillation of the arsenic. A convenient method is to volatilise the germanium in a stream of chlorine gas. Alternatively a few ml. of 28% hydrogen peroxide added to the concentrated HCl will produce sufficient chlorine to keep the arsenic oxidised while the germanium is distilled. After removal of the germanium, the arsenic is reduced by one of the reductants mentioned above and distilled at a temperature below 107°C.

(b) Arsine

Separation as arsine is easily adaptable to rapid procedures. The arsine production may be electrolytic with a mercury (Procedure 11) or graphite (Procedure 21) cathode, or may be by zinc or tin reduction (Procedure 18, 20). Arsenic can be recovered from the arsine gas in a variety of ways, e.g., it can be collected in silver nitrate solution (Procedure 11). After collection, excess silver is removed by precipitation with sodium chloride, and the supernatant made 1 : 1 in HCl. Elementary arsenic is then precipitated by adding ammonium hypophosphite and boiling. Selenium and tellurium can be prevented from reaching the silver nitrate solution by passing the arsine through 10% lead acetate solution first. Alternatively the arsenic can be deposited by heating from the arsine gas as in the Marsh test (Procedure 20 and 21).

(c) Solvent extraction (See also NAS-NS 3102, p. 22)

Several methods of arsenic separation have been developed which make use of solvent extraction. As(III) is extracted 100% from > 8N HCl into benzene (4) with good separation from antimony and bismuth (Fig. 1), or it may be extracted into carbon tetrachloride with diethyldithiocarbamate as complexing agent (5).

Methylisobutylketone extracts 91% of As(III) and 28% of As(V) from a mixture of 8N HCl + 2N H_2SO_4 (6). Fe(III), Sb(V), Sb(III), Sn(III), Sn(IV), Se(IV), Te(IV), Ge(IV), Cr(V), V(V), Mo(VI) and Mn(VI) are also extracted to a greater or lesser extent. Fe(II), Sn(II), Cl(III), Mn(IV), V(IV), Groups IA, IB, IIA, IIB, B, Al, Gp, IVA, Pb, Nb, Ta, P, Bi, Co, Rare Earths, Th and U are not extracted.

As(III) is extracted from HF solutions by ether (7). Sn(IV), Sn(II), Se, Sb and Mo interfere, but there is no extraction of Ni, Cr, Co, Mn, K, Ti, Zr, Ga, Ag, U, Bi, Tl, Cd or Os. It is also extracted from HI solutions by chloroform (8).

Tri-n-butyl phosphate (TBP), and TBP + Tri-n-octylphosphine oxide (Fig. 2) can be used in group separations involving arsenic, but too many other elements are extracted to make a specific procedure possible (9).

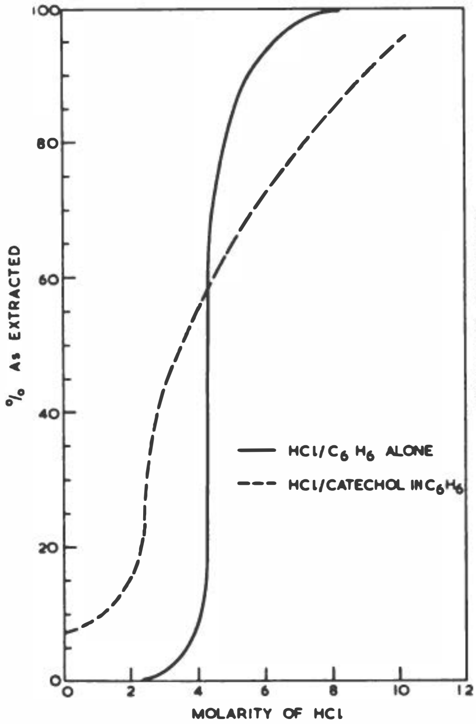


FIG. 1. EXTRACTION OF As (III) FROM HCl

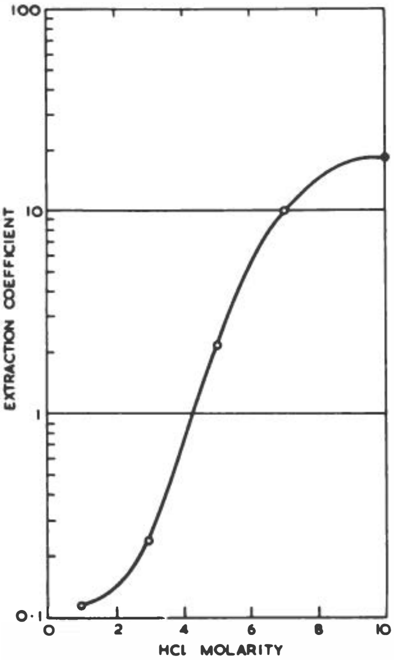


FIG. 2. EXTRACTION OF As (III) WITH TRI-N-OCTYLPHOSPHINE OXIDE As (III) - 1·0mg : TOPO-0·1M IN CYCLOHEXANE, 5 ml : PHASE RATIO-1: EXTRACTION TIME-10m.

(d) Chromatographic methods (See also NAS-NS 3106 p. 38)

Trace quantities of As(III) may be separated from a large number of other ions by electrochromatography (10), and a separation of As(III) from I and Te(IV) by ascending paper chromatography using methanol/water 9 : 1 as solvent has also been reported. (11) Good separation of tracer arsenic from gramme quantities of germanium has also been achieved by reversed phase partition chromatography using HCl elution with TBP as stationary phase. (12)

Finally an anion exchange method using Dowex 1 separated As(V), Se, Ge, Te, Sn, Mo, Re and Au in that order, using various eluants (11.2N HCl for As(V) (13) As(V) does not adsorb appreciably on anion-or cation - exchange resins from HCl solutions and a separation from fission products may be developed on these lines (14).

(e) Precipitation, (Separation, counting and chemical yield)

The most useful arsenic precipitates for separation purposes are the metal and the sulfide. The metal is easily precipitated from hot acid solutions by hypophosphite, 1 : 1 HCl being a most convenient medium. Details of sulfide precipitation have been given in para 1 above.

For counting and chemical yield purposes these two precipitates are also used, together with magnesium ammonium arsenate. The sulfide has the disadvantage that a mixture of As(III) + As(V) sulfide will be precipitated unless care is taken to ensure that all the arsenic is in the trivalent state before preceipitation. The magnesium salt is of rather indeterminate composition and this may introduce an error. On the whole, elemental arsenic is the most satisfactory counting source to use.

IX DISSOLUTION OF ARSENIC SAMPLES

Since arsenic is most easily separated from other elements, except germanium, as the chloride, it would seem that hydrochloric acid would be the logical solvent for an irradiated sample. However, arsenic is unaffected by hydrochloric acid in the absence of oxygen. The element is easily oxidized by oxidizing agents and as hydrogen peroxide, concentrated nitric acid, concentrated perchloric acid, etc. Arsenic will combine directly with chlorine which would result from the oxidation of hydrochloric acid.

Other halides such as the bromide, iodide and fluoride in the presence of an acid, have also been used. Concentrated nitric acid and aqua regia can be used to dissolve the sample provided that sufficient chlorine is present in the solution so that the nitrate ion can be removed by heating.

Many samples can be dissolved in alkali peroxides or an alkali with hydrogen peroxide. This will form the arsenate which can be easily reduced to the As(III) form. Sometimes an easier separation is possible if the arsenic is kept in the higher valence state.

Recent work by Gorsuch on oxidation of biological materials by combinations of nitric and perchloric acids; nitric, perchloric and sulfuric acids; and nitric and sulfuric acids all in the presence of sodium chloride has shown that chloride ion will not cause a loss of arsenic if sufficient nitric acid is initially present. All of the chloride is removed long before there is any chance of the arsenic being reduced to the trivalent form.

X COUNTING TECHNIQUES PERTINENT TO ARSENIC ISOTOPES

In general, the arsenic isotopes emit β^+, β^- particles, γ-rays and x-rays. Standard methods for counting these radiations are used, and readers are advised to consult NAS-NS 3105 for an up to date account of such methods. The paragraphs below attempt to add a few relevant comments on each of the arsenic isotopes.

As^{68} - As^{71}

The very neutron deficient arsenic isotopes are positron emitters, and may be counted either by β-counting, or by counting the 0.511 MeV annihilation radiation. As^{70} has a very prominent annihilation peak, but also has many other γ-rays, giving a rather complicated spectrum, while As^{71} has a prominent γ-ray of 0.175 MeV.

As^{72} - As^{78}

These are, very broadly, the most useful of the arsenic isotopes. As^{72} - As^{76} are produced by (p, n) or (p, γ) reactions on Ge; As^{73} - As^{78} by (n, p) or (γ, p) reactions on Se; As^{77} and As^{78} are fission products. Note also that As^{74} is produced by the (n, 2n) reaction on stable As^{75} while As^{76} is the (n, γ) product of stable As.

As^{72} has a very hard β^+ and a very prominent γ peak at 0.838 MeV together with a large annihilation radiation peak, and so is easily counted. As^{73} decays by electron capture and is rather difficult to count satisfactorily because its soft γ-rays are highly converted. As^{74} emits β^+ and β^- and has a good γ-ray at 0.596 MeV plus annihilation radiation; these are rather close but can be resolved by γ-spectrometry. As^{76} emits a hard, β^- particle, and so is readily counted; it also has a prominent γ-ray at 0.559 MeV. As^{77} is rather more difficult, since its β^- particles are on the soft side and its γ-rays are weak in intensity, the most prominent being at 0.246 MeV. As^{78} is easily counted as it emits hard β^- particles, and has a well defined, fairly hard γ-spectrum.

Some workers have experienced trouble with contamination in these isotopes from Cu^{64}, a 12.8h positron emitter. The annihilation peak of this isotope is very prominent, and careful γ-spectrometry is needed if arsenic isotopes are to be counted by scintillation methods when such contamination is present. Fortunately the half-life of Cu^{64} is sufficiently far from those of the arsenic isotopes that resolution of decay curves is reasonably easy.

As^{79} - As^{81}

These are all short lived isotopes. They are easily counted, since they all emit hard β^- particles. In addition, As^{80} has a prominent γ-ray at 0.66 MeV.

XI. GENERAL REMARKS CONCERNING THE DETAILED RADIOCHEMICAL PROCEDURES OF SECTION XII.

The 21 detailed procedures which follow in section XII fall into only a few main groups, classified according to the principal means of As purification. By far the commonest such means is distillation of either $AsCl_3$ or $AsBr_3$. The principal interfering element is then Ge, but this is easily removed by distilling it off first, having previously oxidised the As to As(V). Having removed the Ge, the As is then reduced to As(III) and distilled in its turn. This is the main purification method in 13 procedures, numbers 1, 2, 4, 5, 6, 7, 8, 9, 10, 12, 13, 15 and 17.

Solvent extraction of AsI_3 into $CHCl_3$ is used in procedure 14 and into C_6H_6 in procedure 19. Anion exchange is used in procedure 16. Precipitation of As_2S_5, with removal of Ge by distillation is used in procedure 3.

The preferred means for the rapid separation of As from complex mixtures is evolution of AsH_3 used in procedures 11, 18, 20 and 21 - the last two taking only 10s and 45s respectively. The procedures use various physical and chemical means for removing other gaseous hydrides which are evolved, (germane stannane and stibine).

It seems probable that almost any particular purification requirement can be met by one or other of these methods, or by some combination of them.

XII COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES

(arranged in chronological order)

Procedure 1

Procedure by: J. W. Irvine; J. Phys. Chem. 46, 810 (1942)

Type pf procedure:	With carrier
Target material:	Cyclotron targets
Radioactivity production method:	Cyclotron bombardment
Purification method:	Distillation of $AsCl_3$.
Approx. chemical yield:	High
Time taken for procedure:	Not given
Decontamination:	"Free from radioactive contamination".

1. Place target material in Claisen flask and add 0.5-2 mg sodium arsenite carrier. Add 25 ml. 12 M HCl heat and add 30% H_2O_2 dropwise until target is dissolved (10-20 ml H_2O_2 needed and the operation takes ~ 5m).

2. Distil off Ge with frequent addition of a few drops of H_2O_2 to minimise reduction of As(V) to As(III) with consequent loss of $AsCl_3$. When solids precipitate from the solution in the flask add 10 ml 12 M HCl and repeat the distillation. Add glass beads or tile to prevent bumping if necessary.

3. Add 15 ml 12 M HCl and then 10 ml 5 M HBr to reduce As(V) to As(III) and distil As into 10 ml of distilled water in an ice bath until bromine fumes appear. Add 10 ml 12 M HCl + 5 ml 5 M HBr and repeat distillation until bromine fumes again appear.

4. Precipitate As metal from distillate by adding 1-2 g solid ammonium hypophosphite and warming on a steam bath 5-10 m. Do not heat too long or precipitate will coagulate too much: if this happens add a few mg of Duponol or other wetting agent.

5. Filter without allowing air to be sucked through the precipitate until it has been washed with 5-10 ml freshly boiled distilled water and with acetone. (This prevents oxidation).

Procedure 2

Procedure by: H. Lanz and J. G. Hamilton, U.S.A.E.C. unpublished report MDDC 1596 (1948).

Type of procedure:	Carrier free
Target material:	Ge metal
Radioactivity production method:	19 MeV deuterons
Purification method:	Distillation of $AsCl_3$.
Approx. chemical yield:	Not given
Time taken for procedure:	Not given
Decontamination:	Not given

1. After cooling for several days, dissolve Ge metal by refluxing in aqua regia for 24 h.

2. Add excess HCl to destroy HNO_3, bubble chlorine gas through to keep As in pentavalent state, and carry out four distillations of $GeCl_4$ from solution, 7N HCl being added each time just before solution goes to dryness. On last distillation add 50 mg Ge carrier to ensure a complete removal of radioactive Ge.

3. Stop chlorine stream, add 48% HBr and distil off $AsCl_3$ and collect in conc. HNO_3. Two HBr distillations are needed to ensure complete As removal.

4. Evaporate HNO_3 distillate to dryness on a steam bath, converting As to arsenic acid. Take up As residue in 0.1 N HCl.

Procedure 3

Procedure by: H. Hopkins; Reported by W.W. Meinke, U.S.A.E.C. unpublished report UCRL-432 Procedure 33-1. (1949).

Type of procedure:	With carrier
Target material:	As metal
Radioactivity production method:	190 MeV deuterons
Purification method:	As_2S_5 precipitation + Ge distilation.
Approx. chemical yield:	~ 80%.
Time taken for procedure:	1 h.
Decontamination:	Radiochemically pure by factor of ~ 100.

1. Dissolve As in conc. HNO_3 + HCl. Add carriers of Se and elements below (2 mg).

2. Evaporate to near dryness to remove excess HNO_3, Make up to 5 ml with 1 N HCl, add $NH_2OH.HCl$ until Se starts to precipitate from hot solution. Add 1 ml 1 N KI, heat 5 m, and centrifuge off Se.

3. Add HCl to make 3 N solution containing 10 mg As/ml.

4. Pass H_2S take hot solution and stir vigorously. Repeat.

5. Centrifuge off precipitate and wash with water.

6. Dissolve As and Ge salts with dilute KOH, leaving CuS behind.

7. Separate Ge by distilling from 20 ml of boiling 6N HCl in a slow stream of chlorine. When ¼ volume remains, add 6N HCl and repeat.

8. Precipitate As_2S_5 from 3N HCl.

Remarks: Se and As may first be removed together by volatilising the elements along a quartz or pyrex tube.

Procedure 4

Procedure by: H. Goeckermann; Reported by W.W. Meinke, U.S.A.E.C. unpublished report UCRL-432, Procedure 33-2 (1949).

Type of procedure:	With carrier
Target material:	~ 1g Bi metal
Radioactivity production method:	184" cyclotron, all particles.
Purification method:	Distillation of $AsCl_3$ + sulfide precipitation.
Approx. chemical yield:	Not given.
Time taken for procedure:	Few hrs.
Decontamination:	Factor ~ 10^4 from fission and spallation products.

1. To aliquot of HNO_3 solution of target, add 10 mg As and ~ 10 mg Ge carriers: boil nearly to dryness, take up in 15 ml 6N HCl, add crystal of NH_4I, and saturate with H_2S at ice temperature: wash with H_2S saturated 6N H_2SO_4.

2. Dissolve precipitate in 1 ml conc. NH_4OH and dilute to 10 ml (discard any residue). Transfer to a glass still and add ~ 10 mg each of Te, Sb and Sn carriers. Add 10 ml conc. HCl and distil all but 5 ml in a chlorine stream into 5 ml water in an ice bath. Add 5 ml conc. HCl and ~ 10 mg Ge to residue in flask and repeat distillation.

3. To residue from $GeCl_4$ distillation, pass in HCl gas to remove Cl_2, add 1 ml saturated CuCl in conc. HCl, and distil over 5 ml in an HCl stream into 10 ml conc. HCl in an ice bath. Add CuCl-HCl to residue and distil further.

4. Pass H_2S into distillate and centrifuge out As_2S_3. Dissolve in 1 ml conc. NH_4OH, add ~ 10 mg Te, Sb and Sn carriers and repeat $AsCl_3$ distillation.

5. Precipitate As_2S_3 again, dissolve in 1 ml conc. NH_4OH, add 10 ml conc. HCl, saturate with H_2S, filter, wash with water, ethyl alcohol and ether, dry 10 min at 110°C. Weigh as As_2S_3 (16.4 mg per 10 mg As).

Remarks: Cylinder HCl and Cl_2 are rather unpleasant and corrosive to work with. Procedure is fairly slow. Ge can be separated along with As as indicated.

Procedure 5

Procedure by: A.S. Newton: Reported by W.W. Meinke, U.S.A.E.C. unpublished report UCRL-432, Procedure 33-3 (1949).

Type of procedure:	With carrier
Target material:	0.1-1g Th. metal
Radioactivity production method:	60" cyclotron α particles
Purification method:	Distillation of $AsCl_3$.
Approx. chemical yield:	Undetermined.
Time taken for procedure:	~ 2-3 h.
Decontamination:	10^5-10^6.

1. Dissolve Th metal in conc. HCl + a few drops 0.2 M $(NH_4)_2SiF_6$ to clear up black residue: Dilute HCl to 2N and take aliquot.

2. Add 10 mg Ge and As carriers and make up to 15 ml. 6N in HCl. Add crystal of NH_4I and treat with H_2S at ice temperature. Wash with 6N H_2SO_4 saturated with H_2S.

3. Dissolve precipitate in 1 ml conc. NH_4OH and dilute to 10 ml. Discard any residue. Transfer to glass still and add 10 mg each of Te, Sb and Sn carriers. Add 10 ml conc. HCl and a crystal of $KClO_3$. Distil all but 5 ml into 5 ml water in an ice bath.

4. Add 5 ml conc. HCl, 10 ml Ge carrier and $KClO_3$ to remaining solution in still and repeat.

5. To residue from $GeCl_4$ distillation, pass in HCl gas to remove Cl_2.

6. Add 1 ml saturated CuCl solution in conc. HCl and distil over 5 ml in HCl stream into 10 ml conc. HCl in ice bath.

7. Add CuCl -HCl and distil again. Pass H_2S into distillate and precipitate As_2S_3.

8. Dissolve in 1 ml conc. NH_4OH, add 10 mg. Te, Sb and Sn carriers and repeat distillation. Precipitate As_2S_3 again, dissolve in 1 ml conc. NH_4OH, add 10 ml conc. HCl saturated with H_2S. Filter, wash with water, ethy alcohol and ether. Dry at 110°. Weigh as As_2S_3.

Procedure 6

Procedure by: L. Winsberg, Radiochemical studies: the fission products; Book 3, Paper 228, pp. 1440; McGraw-Hill; New York, 1951.

Type of procedure:	With carrier
Target material:	Freshly irradiated uranium
Radioactivity production method:	Reactor neutrons
Purification method:	Distillation of $AsCl_3$
Approx. chemical yield:	Not given.
Time taken for procedure:	Not given.
Decontamination:	$>10^6$ for As^{77}.

1. To an appropriate amount of neutron-irradiated uranyl nitrate solution in a 50 ml centrifuge tube, add 2 ml each of standardised Ge and As carrier solution and boil nearly to dryness to remove excess HNO_3. Take up in 15 ml 6N HCl, place in an ice bath, and pass in H_2S, adding a few crystals of NH_4I to aid precipitation if necessary.

2. Dissolve mixed precipitate in 1 ml conc. NH_4OH and dilute to 10 ml, add 0.5 ml Zr carrier solution. Centrifuge and discard $Zr(OH)_4$ precipitate. Add 10 ml conc. HCl and pass in H_2S. Centrifuge and wash the precipitate with 10-15 ml. of H_2SO_4-H_2S solution. Add 5 ml H_2O and heat to expel excess H_2S. Add 1 ml conc. NH_4OH to dissolve any GeS_2 or As_2S_3 remaining, and transfer to a still. Add 10 mg. each of Te, Sb and Sn carriers. (Disregard the sulfides that form in the still).

3. Add 10 ml. conc. HCl, pass in Cl_2 gas, and distil all but 5 ml. of the solution into a centrifuge tube containing 5 ml. of H_2O cooled in an ice bath. Set aside the distillate for Ge separation, if desired.

4. Add 5 ml. conc. HCl and 1 ml. Ge carrier solution, and distil $GeCl_4$ again, as in step 3.

5. Remove Cl_2 gas, and pass in air. Add 1 ml. of a saturated solution of CuCl in conc. HCl and 5 ml. conc. HCl and distil to about 1 ml., taking care not to heat to dryness or Sb may distil. Add 5 ml. of conc. HCl and 1 ml. of CuCl-HCl solution, and distil again to about 1 ml. Catch the distillates in 10 ml. of H_2O in a centrifuge tube cooled in an ice bath.

6. Pass H_2S into the combined distillate to precipitate As_2S_3. Centrifuge, dissolve in 1 ml. NH_4OH, add 10 mg. each Te, Sb and Sn and distil as in step 5.

7. Precipitate the As in the distillate as As_2S_3, dissolve in 1 ml. conc. NH_4OH and dilute to 10 ml. (If a precipitate returns, centrifuge and discard it). Add 10 ml. conc. HCl, pass in H_2S to complete the precipitation and then filter. Wash several times with H_2O, ethyl alcohol, and ether. Dry at 110° for 10 m. Weigh as As_2S_3.

Procedure 7

Procedure by; A. A. Smales and B. D. Pate: Anal. Chem. 24 717 (1952).

Type of procedure:	With carrier
Target material:	General samples, including GeO_2.
Radioactivity production method:	Reactor neutrons
Purification method:	Distillation of $AsCl_3$.
Approx. chemical yield:	Not given
Time taken for procedure:	Not given
Decontamination:	Not given

1. Irradiate simultaneously for period of up to 30 h., sealed silica containers, each about 0.5 ml capacity and containing a weighed amount (approx. 0.1 ml.) of the solution under test, and also one containing standard arsenic solution (1 μg As/ml). Transfer contents of each silica container to a distillation flask together with ~ 0.5 g NaOH.

2. Add by pipette 5 ml. sodium arsenite solution containing 10 mg As/ml and wash this, together with a few drops of H_2O_2 solution through the dropping funnel into the flask. Warm gently and add gradually via the dropping funnel 10 ml. conc. HCl to which has been added 5 ml. of 30% H_2O_2, followed by a little distilled water.

3. Distil down to 2-3 ml., adding H_2O_2 dropwise from time to time. Repeat twice more the addition of acid and peroxide and distillation to a small volume.

4. Add 10 ml. 40% HBr and distil $AsCl_3$ into 10 ml. cold water. Distil to low volume and repeat addition of HBr and distillation twice more.

5. Add to distillate a few mg of Ge carrier and 1/2 g solid ammonium hypophosphite: heat to 90-95°C for 30 m to precipitate and coagulate As metal.

6. Centrifuge, wash with water and mount.

7. Standard and sample are counted under identical conditions to reduce counting corrections.

Procedure 8

Procedure by: A. A. Smales and B. D. Pate: Analyst 77 188 (1952)

Type of procedure:	With carrier
Target material:	Sea water + trace As
Radioactivity production method:	Reactor neutrons.
Purification method:	Distillation of $AsCl_3$
Approx. chemical yield:	Not given
Time taken for procedure:	Not given
Decontamination:	Not given

1. Transfer activated sea water sample to the distillation flask and add 1 ml 10% NaOH solution, followed by 5.0 ml of sodium arsenite carrier solution (10 mg As/ml). Add a few drops 30% H_2O_2 and wash down dropping funnel with a little water. Reduce volume to ~ 2 ml by boiling and add a mixture of 10 ml conc. HCl + 5 ml 30% H_2O_2 which is freely evolving chlorine. Distil to 2 ml. This procedure destroys any organic-arsenic compounds which may be present.

2. The remainder of the procedure is identical with steps 4-7 of procedure 7.

Procedure 9

Procedure by: A. A. Samles and B. D. Pate; Analyst 77 196 (1952).

Type of procedure:	With carrier
Target material:	Biological material + trace As
Radioactivity production method:	Reactor neutrons
Purification method:	Distillation of $AsCl_3$
Approx. chemical yield:	Not given
Time taken for procedure:	Not given
Decontamination:	Not given

1. Transfer weighed sample after irradiation to a 250 ml beaker. Add 5.0 ml of a standard arsenic solution (10 mg/ml As) followed by 2 ml 30% H_2O_2, 5 ml HNO_3 (S.G. 1.42), 5 ml H_2SO_4 (S.G. 1.84) and 2 ml $HClO_4$. Gently heat solution until initial reaction subsides and then more strongly, adding further HNO_3 if necessary to prevent charring. Finally heat until H_2SO_4 + $HClO_4$ fumes appear and until all organic matter is completely oxidised.

2. Dilute, after cooling, to 20 ml, add 20 ml HCl (S.G. 1.19) and precipitate As by adding 1g solid ammonium hypophosphite and heating to 90-95°C to coagulate As.

3. Centrifuge of precipitate, wash with water, and dissolve by adding 5 ml water, 2 ml H_2O_2 and 2 ml HCl. Transfer solution to distillation vessel and proceed with distillation etc. as in procedure 7.

Procedure 10

Procedure by: L. Salmon; U.K.A.E.A. unpublished report AERE C/M 154 (1952).

Type of procedure:	With carrier
Target material:	Sulfur + trace As.
Radioactivity production method:	Reactor neutrons
Purification method:	Distillation of $AsCl_3$
Approx. chemical yield:	Not given
Time taken for procedure:	Not given
Decontamination:	Not given

1. Dissolve sulfur target in a mixture containing 10 ml CCl_4, 1 ml bromine, 5 ml HNO_3 (S.G. 1.42) and 5.0 ml. As carrier (made by dissolving 1.32g As_2O_3 in a little NaOH and making up to 100 ml with water: 1 ml = 10.0 mg As). Warm gently until all sulfur is dissolved, evaporate off CCl_4+ bromine gently and finally evaporate to fumes of H_2SO_4. Cool, add, 5 ml water and 1 ml 3N NaOH. Transfer to distillation flask.

2. Distil down to 2 ml and reject distillate. Add 10 ml conc. HCl + 5 ml 100 vol H_2O_2. Again evaporate to 2 ml and reject distillate.

3. Add 10 ml 40% HBr and distil into 10 ml of cold water. Repeat with 10 ml of HBr twice more.

4. Add 1-2g solid ammonium hypophosphite to distillate and warm to 90°-95° for 30 m to precipitate As metal. Centrifuge and wash with water. Mount.

Procedure 11

Procedure by: J. G. Cuninghame; Phil. Mag. 44 900 (1953).

Type of procedure:	With carrier
Target material:	Natural uranium
Radioactivity production method:	Reactor neutrons
Purification method:	Evolution of AsH_3 + $AsCl_3$ distillation
Approx. chemical yield:	35%
Time taken for procedure:	45m
Decontamination:	Gives radiochemically pure As^{77}, As^{78} and As^{79} from fresh mixed fission products.

1. Add irradiated uranium solution to standardised arsenite carrier in dilute H_2SO_4, oxidise to As(V) with potassium bromate and then reduce to As(III) with potassium metabisulphite.

2. Place in operating arsine generator with mercury cathode* and generate arsine for 15 m with cell at ~ 80°C at cathode current density of ~ 2.5 amp/cm^2. Pass AsH_3 through lead acetate solution to absorb any Se and Te and collect in $AgNO_3$.

3. Add Sb carrier to $AgNO_3$, followed by NaCl, filter and carry out ferric hydroxide scavenge on supernate.

4. Make supernate 1:1 in HCl and add Sb hold back carrier. Precipitate As metal by adding ~ 1g solid ammonium hypophosphite and bringing solution to the boil.

5. Dissolve As metal in brominated HCl and distil As from concentrated HBr in presence of Sb, Te and Sn hold-back carriers. Collect As in concentrated HCl.

6. Reprecipitate As metal, filter and mount.

* As used by D. Rogers and A. E. Heron; Analyst 71 4 '4 (1946).

Procedure 12

Procedure by: J. A. James and D. H. Richards: Anal. Chem. Acta 15 118 (1956).

Type of procedure:	With carrier
Target material:	Tungsten metal + trace As
Radioactivity production method:	Reactor neutrons
Purification method:	Distillation of $AsCl_3$
Approx. chemical yield:	Not given
Time taken for procedure:	Not given
Decontamination:	Not given

1. Irradiate simultaneously W sample and As standard. Transfer W sample to $KOH-H_2O_2$ mixture containing 60mg As_2O_3 carrier and warm until dissolution complete (~ 30 m).

2. Distil to low volume, discard distillate, acidify with $HCl-H_2O_2$, and again distil to low volume. Discard distillate.

3. Add HBr and distil into cold water.

4. Take distillate, add inactive WO_3 and repeat the HBr distillation.

5. Add a solution of sodium tungstate complexed with excess tartaric acid to distillate, then add solid ammonium hypophosphite and boil for 30 m to coagulate As. Centrifuge and mount.

6. Dissolve the As standard into a $KOH-H_2O_2$ solution containing a known amount of ~ 100 mg As_2O_3 and make up to 100 ml. Take a suitable aliquot of this solution and add to an alkaline peroxide solution containing 60 mg As_2O_3. Precipitate As and mount as in step 5.

Procedure 13

Procedure by; O.R.N.L. Master Analytical Manual Method 5-110600 (1957).

Type of procedure:	With carrier
Target material:	Metals, alloys, fine chemicals, other solid materials or liquids + trace As.
Radioactivity production method:	Reactor neutrons
Purification method:	$AsCl_3$ distillation + As_2S_3 precipitation.
Approx. chemical yield:	70%
Time taken for procedure:	Not given
Decontamination:	"Adequate"

1. Irradiate sample and standard As_2O_3 simultaneously and prepare for analysis as follows:-

   (a) Metals, alloys, fine chemicals, or other solid materials

   Transfer to 60 ml distilling flask and pipette in 2 ml standard As carrier solution. Add 25 ml conc. HCl and heat to dissolve: during dissolving make repeated dropwise additions of 30% H_2O_2 until sample is completely dissolved.

   (b) Liquid samples

   Pipette aliquot into 60 ml distilling flask and add 2 ml standard As carrier.

   (c) Standard As_2O_3

   Place 100 mg As_2O_3 in 100 ml volumetric flask, dissolve in 2M NaOH and dilute to mark. Mix, take aliquot and add to distilling flask, together with 2 ml standard As carrier.

2. Add to distilling flask 2-5 mg each of Fe, Co,Cu, Sr and Na carriers. Add 15 ml conc. HCl + 10 ml 5M HBr and distil into 10 ml of water in an ice bath. When bromine fumes appear in distillate add 10 ml conc. HCl + 5 ml 5M HBr to distilling flask and distil again.

3. Make distillate 1M in HCl and precipitate As_2S_3. Wash precipitate with 1M HCl.

4. Dissolve in small amount conc. HNO_3; add 5 mg Se carrier and evaporate to dryness to remove excess HNO_3. Take up in 10 ml 1M HCl heat to near boiling and add 5M hydroxylamine hydrochloride dropwise until all Se is precipitated. Allow precipitate to settle and add a further 5 mg of Se. Centrifuge and wash with two 5 ml portions of hot water. Add washes to supernate.

5. Add 5 mg Sb carrier to combined supernate and add enough conc. HF to make 7M in HF by adding conc. HF. Cool and precipitate As_2S_3. Wash with two 5 ml portions of water.

6. Precipitation of As

(a) As_2S_3

Dissolve precipitate from step 5 in 1 ml. conc. NH_4OH. Add 10 ml conc. HCl. Precipitate with H_2S; wash with three 5 ml portions of water and three 5 ml portions absolute ethanol; dry at 110° for 15 m.

(b) $MgNH_4AsO_4.H_2O$

(i) Dissolve precipitate from step 5 in 5 ml. conc. HNO_3, transfer to 50 ml beaker and add 1-2 ml. bromine water. Heat to destroy sulfur and oxidise to As(V).

(ii) Cool and add 10 ml. magnesium mixture to the solution. Neutralise with conc. NH_4OH and add excess until a precipitate forms. Digest 15 m.

(iii) Filter and wash with three 5 ml. portions 2.5% NH_4OH, three 5 ml. portions of absolute ethanol and three 5 ml. portions ether. Dry at 110° for 30 m. Weigh as $MgNH_4AsO_4.½ H_2O$.

(c) As metal

(i) Dissolve precipitate from step 5 in 0.5 ml. conc. HCl + 0.5 ml. conc. HNO_3 + 1.0 ml. $HClO_4$. Heat for 5 m and fume. When fumes arise from top of tube, discontinue heating.

(ii) Cool and add 10 ml. 6M HCl. Heat to boiling and add 5 ml. $CrCl_2$. Digest in steam bath until precipitate forms, then add additional 5 ml. $CrCl_2$. Heat 5 m more.

(iii) Filter, wash with three 5 ml. portions water and three 5 ml. portions absolute ethanol. Dry at 110° for 15 m.

Procedure 14

Procedure by: R. J. Prestwood; U.S.A.E.C. Unpublished report LA 1721 2nd ed. (1958).

Type of procedure:	With carrier
Target material:	Fissile material
Radioactivity production method:	Fission
Purification method:	Extraction of AsI_3 into $CHCl_3$ + As_2S_3 precipitation.
Approx. chemical yield:	80%
Time taken for procedure:	4h for quadruplicate analyses.
Decontamination:	~ 6000

1. Make sample acid and precipitate As_2S_3. Chief contaminants are Ge, Te, Mo and Cd. Fume with mixture of $HNO_3/HCl/HClO_4$ to remove Ge.

2. Convert As to tri-iodide by treatment with HI and extract into $CHCl_3$; Te, Mo and Cd are not extracted; the decontamination in this step is ~ 6000.

3. Wash solvent phase and back-extract As with dilute H_2SO_4. Repeat extraction and back-extraction.

4. Precipitate As_2S_3 and dissolve. Precipitate As by adding $CrCl_2$ and mount.

Procedure 15

Procedure by: G. F. Shipman and O. I. Milner; Anal. Chem. 30 211 (1958).

Type of procedure:	With carrier
Target material:	Hydrocarbon reforming catalyst + trace As
Radioactivity production method:	Reactor neutrons
Purification method:	Distillation of $AsBr_3$
Approx. chemical yield:	Not given
Time taken for procedure:	15 h for batch of four samples
Decontamination:	Not given

1. Place sample into nickel crucible and weigh. For each gramme of sample, add 10g Na_2O_2, mix intimately, and sprinkle a layer of Na_2O_2 on top of the mixture. Place in a muffle furnace at $500^o \pm 25^oC$ for 1 h. Remove, cool and leach with ~ 30 ml water. Add 1:1 H_2SO_4 cautiously until precipitate of aluminium hydroxide redissolves and then add 5 ml excess. Transfer to 50 ml volumetric flask, cool and make up to the mark.

2. Place 20 ml conc. H_2SO_4 in a distilling flask and add 2.00 ml of carrier As solution (5.00 mg As/ml.) and an aliquot of the sample sufficient to give a final activity of 10,000 c.p.m. Rinse with two 2 ml washes. Finally add 2 ml 47% HBr. Bubble nitrogen at a rate of 1 bubble/s. Heat to 120^o, and stop distillation when temperature begins to fall.

3. Make distillate 7-8N in HCl and add 2-3g ammonium hypophosphite. Digest in steam bath 45 m. Filter and mount.

Procedure 16

Procedure by: U. Schindewolf and J. W. Irvine; Anal. Chem. 30 906 (1958).

Type of procedure:	Carrier free
Target material:	Ge
Radioactivity production method:	Cyclotron
Purification method:	Anion exchange
Approx. chemical yield:	Not given
Time taken for purification:	Not given
Decontamination:	Estimated as $>10^7$ from 6c

1. Dissolve Ge target in a few ml of conc. HCl/HNO_3, heating in a steam bath if necessary.

2. Reduce As(V) and excess acid with SO_2 and dilute to 0.25-2.5M HCl.

3. Pass through anion exchange column equilibrated with dilute HF. For absorption of 1g of Ge, use a column 1.3 cm diameter, 25 cm. long. Elute As with about 5 column volumes of dilute HF. Concentrate eluate in steam bath if desired.

Note: Volatile AsF_3 does not form as long as a liquid phase is present. However, with the disappearance of the last drop of solution, there is a substantial loss of activity. This loss can be eliminated by adding 1 ml. conc. HNO_3 to the solution to oxidise As to As(V), which remains on evaporation to dryness.

Procedure 17

Procedure by: I. J. Gruverman & P. Kruger; Inter. J. Appl. Rad. and Isotopes 5 28 (1959).

Type of procedure:	Carrier free
Target material:	Ge
Radioactivity production method:	$Ge^{72}(d,n)As^{73}$: $Ge^{73}(d,2n)As^{73}$: $Ge^{73}(d,n)As^{74}$: $Ge^{74}(d,2n)As^{74}$.
Purification method:	Distillation of $AsCl_3$
Approx. chemical yield:	Recovery 90%
Time taken for purification:	Not given
Decontamination:	Product 98% (As^{73} + As^{74}).

1. Age Ge target, about 5g, 10-15 days to allow As^{71} to decay and dissolve in aqua regia. Evaporate nearly to dryness twice while passing chlorine gas through rapidly.

2. Dilute with 15 ml HCl and transfer to distilling flask. Distil Ge into trap containing 6N NaOH while passing chlorine through still. Evaporate to near dryness several times, with additions of HCl between evaporations. A total of 25-35 ml is distilled.

3. Now distil As into ice-cooled water trap by adding 5 ml of a saturated solution of CuCl to the still and passing HCl gas through. Continue distillation until activity cannot be detected in the still.

4. Evaporate active distillate to desired volume while bubbling chlorine into the liquid.

Procedure 18

Procedure by: H. Smith; Anal. Chem. 31 1362 (1959).

Type of procedure:	With carrier
Target material:	Biological tissue + trace As
Radioactivity production method:	Reactor neutrons
Purification method:	Evolution of AsH_3
Approx. chemical yield:	Not given
Time taken for purification:	Not given
Decontamination:	Not given

1. Wash digested sample into 200 ml. flask and add 10 μg. As carrier, followed by 2 ml. conc. H_2SO_4, 4 ml. conc. HCl, 5 ml of a 15% solution of NaI, and 0.4 ml. of a 40% solution $SnCl_2$ in 50% HCl. Dilute to 150 ml. and place in water bath for 5m.

2. Add 10g 16-22 mesh zinc pellets and allow evolution of hydrogen to continue 15m. Pass evolved AsH_3 through lead acetate on a cotton wool filter, and collect As in 1 ml. of a 1.6% solution of Hg Cl_2. Add 5 ml. of 0.001 N iodine in 40% NaI solution to help solution of any solids formed. Wash delivery tube well into trap.

Procedure 19

Procedure by: A. Kjelberg & A. C. Pappas; J. Inorg. Nucl. Chem. 11 173 (1959).

Type of procedure:	With carrier
Target material:	2.0g uranyl nitrate
Radioactivity production method:	Reactor neutrons
Purification method:	C_6H_6 extraction
Approx. chemical yield:	Not given
Time taken for purification:	~ 2m for separation from Ge by solvent extraction steps. Time not given for full procedure.
Decontamination:	$> 10^6$ for Ge: "sufficient" for other fission products.

1. Dissolve sample (without heating) in 6.5 ml water to which is added 20 mg Ba + 20 mg As(V) carriers and 3 drops conc. HCl. Transfer to separating funnel containing 20 ml. C_6H_6. Add 4.5 ml. 10.2 N HI (commercial 67%) and shake 10 s. Reserve aqueous for Ba.

2. Back extract with 6.5 ml. water for 30 s and wash aqueous phase with 10 ml C_6H_6 for 5 s.

3. Repeat extraction and back extraction.

4. Add 10 mg Te(IV) carrier + 3.5 ml conc. HCl. Heat nearly to boiling and reduce with SO_2. Filter Te and boil supernate to drive off SO_2. Cool and add 20 ml. conc. HCl.

5. Precipitate As with H_2S, centrifuge, and wash with 6N HCl saturated with H_2S.

6. Dissolve sulfide in 0.5 ml conc. HCl + 0.5 ml conc. HNO_3 + 1.0 ml $HClO_4$, heat in water bath 5 m and then to strong fumes. Cool.

7. Re-extract with C_6H_6 and back extract as in steps 1 and 2.

8. Reprecipitate As as sulfide and redissolve. Dilute to 20 ml with 6N HCl and precipitate As metal by adding 100 mg KI + 1g sodium hypophosphite, and heat until coagulated. Wash with hot water and mount.

Procedure 20

Procedure by: A. E. Greendale & D. L. Love; Anal. Chem. 35 632 (1963).

Type of procedure:	With carrier
Target material:	Fissile material
Radioactivity production method:	Reactor neutrons
Purification method:	Evolution of AsH_3

Approx. chemical yield:	70-80%
Time taken for purification:	10 s.
Decontamination:	Mixed fission products (2 weeks old) 10^7; Sb 2×10^3; Sn $= \sim 10^6$.

1. Add sample to 4 ml. of a 30% solution of H_2SO_4 containing 1 mg each Sb and As carriers.

2. Drop solution into flask containing 5g granular zinc held at 100°C in a water bath, with dry nitrogen flushing through.

3. Pass $N_2 + SbH_3 + AsH_3$ through a tube of drying agent, followed by a quartz tube in a furnace held at 600°C. The Sb metal deposits on this tube and on a sintered glass filter which follows it. The As metal deposits on a second quartz tube heated to a reddish glow by a burner, which follows the sinter.

Procedure 21

Procedure by: L. Tomlinson; Anal. Chim. Acta, 32 157 (1965).

Type of Procedure:	With carrier
Target material:	Fissile material
Radioactivity production method:	Reactor neutrons
Purification method:	Evolution of AsH_3
Approx. chemical yields:	$\sim$ 50%
Time taken for purification:	$\sim$ 45 s.
Decontamination:	Br $> 3 \times 10^3$: I $> 4 \times 10^4$; Te 2×10^5; Se 9×10^4; Sn 2×10^3; Sb 2.5×10^3; Ge not measured.

1. Dissolve radioactive mixture containing As in HCl or H_2SO_4 and add 0.5mg Sb(III) ($SbCl_3$ dissolved in HCl) and 0.5 mg As(III) (As_2O_3 dissolved in NaOH solution and excess HCl added). Adjust acidity to 5N and volume to 5.5 ml.

2. Add mixture to the cathode compartment of a diaphragm type electrolytic cell having a graphite cathode and a platinum gauze anode through whose cathode compartment pure He or N_2 has been flowing for several minutes at 250 ml/m.

3. Pass a current of 50 amps for 10 s, flush for a further period and turn off gas flow.

4. The mixture of carrier gas, hydrogen, arsine, stibine, germane and stannane passes out from the cell and through a calcium sulphate column which removes any moisture and most of the stannane, a silica tube at 480°C followed by a 40 m.m. diameter sintered glass filter of 20-30 μ pore size on which is deposited Sb and Ge, and then through a second silica tube and sinter at 950°C on which metallic As is deposited as a mirror.

5. Count As in situ or dissolve in HCl/H_2O_2 and count as a liquid, or reprecipitated As metal.

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