TABLE 2a. DECAY CJIAINS AND IlBLDS OP GERMANIUM

# NUCLI.Dl3S PROM 'l'HBRMAL-NEUTRON FISSION OP ua3s•

'

49-h zn

14.1-h Ga.72

--} sta.ble Ge72

(1,2)

l.6ll:10-5

72

(<2-m zn73) --+ 5.0-h Ga73 --+ stable Ge73

1.1x10-4

(-2)

54-s Ge77'JII.

l

0.22

12-h Ge77

0.0031

* 38. 7-h As 77 --j> stable Se77

0 • 0083

(3,4)

86-n. Ge7 >

78

91-m AS

--}

78 •

stable Se

TABLB 2b. 'IOTAL CUMUIATIVB YIELDS OP

Ge77\_PROM u,'l'h AND Pu

u-233 Pu239

Pu239 u235 u238

n,.232

Th232

(therma1) (therlllll.1) (fast) (14 Mev) **(£ast)**

(l, )

(fut)

(S)

(~8 **Mev)**

(6)

12-h Ge77

0.010

0.009 0.022

•Reproduced.from Nucleo11ics Data Sheet No. 24, "Piaaiou-Product Yields from u, Th, and Pu,11 authored by s. lCatcoff, Hueleonics 16, No. 4, pp. 78-85, 1958.

1. RBVIBW OP CHEMISTRY OP G.RRMANillM OP INTBRBST TO RADIOCHJ!MISTS
   1. Meta.llic Germanium

Germanium is a relatively uncommon substance **making** up about

10-11 percent of the earth's crust. lt was discovered in the

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mineral a.rgyrodite, 4Ag •Ges2• It•s chief occ rence is in cer­

tam zinc blendea **and a** major source of supply is by-product

·obtained in the smelting of zinc.

The element resembles ce.rbon and silicon in having the ns2np2 electron configuration and 3P ground stat and in forming the

tetrahedral bonds associated with sp3 hybridization. Blementary gerlll&liium **posaesses** the diamond atructure that characterizes ca..rbon\_t silico11 and gray tin. An e.inor.phous for111 is also known, Germanium, lilce silicon, ia a semico.ndu tor. In tbe purest form it has a specific resistance at room teioperature of about 50 ohm/cm the resistivity decreasing with ris:ing temperature.

The metal is silvery-white, be.rd llJld brittle. It melts at

*9.59°c* and boils at 2100°c. Additional. properties of the metal are:

|  |  |  |
| --- | --- | --- |
| Density | (g/cc) | 5.36 |
| Atomic Vol-uae | | *13.55* |
| Ionization Potential (ev) | | 8.13 |
| Cev) | | 15.86 |
| Atomlc Radius (A0) | | 1.22 |
| Ionic **Radius .M4•** CA0) | | 0.53 |
| Specific **Heat** (cal/g) | | 0.074 |
| Hardness (Nob's Scale) | | 6.0-6.5 |

Ger11uu1ium is .only pattially deposited by elec·trolysis of acid solutions. Bl-ectrolysis **wi .lt a** mercury cathode in dilute su1furic acid solutiOD., however, apparentiy quantitively deposits **germanium.** in

the •ercury cathode.(?) It deposits c011pletely from-alkaline solu ions containing oxalate, t&.rtrate, ph sphate, carbonate or hydroxide ion ii.swell. Careful control of conditions is required

to obtain a bright adherent deposit. Blectrodeposition of **germBJ1i11111**

from sol-utions·o(**- eI4** in ethylene- .glyc lCS)and GeC14 in propylene glycol(g) p oduces·a.thick met&llic film. Blectrolysis of **a** solu-

6.

.





tion of germanium (IV) oxide in fused borax(S).or potusiUJI. or sodium carbonate lso deposits the metal.

Germanium metal may also be prepared by reduction of germanium

(IV) oxide by carbon or by l'llixed potassium cy\_auide and carbon under a molten sodiUIII chloride flux. Ger■aniWIICII) oxide sublimes at 710°c and the layer of fued chloride prevents excessive losses

of the element due to its volatility. Reduction witb hydro en ca:n be c:arried out at temperatures as low as 5oo0c t·llereby removing tbe necessity for protective fused salt blanket.

Very pure germaniQ.111 is made by the metho of zone refining.

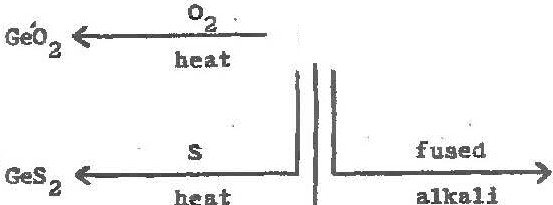
Germaniun **metal** ls not appz,ec ably affected by water, fifty percent sodium hydroxide, hydrochloric acid, suif ic acid and hydroflouric acid. It is·tarniahed by ten percent sodiWll hydroxide and concentrated nitric acid. Diiute nitric **acid forma a germanium** (IV)·oxide fil on the metal. The metal is dissolved by three percent hydrogen peroxide.

* The incipal reactions of germanium are as shown in Pigure

2 below.

Pigure 2. The Principal Reactions of **Germanium**

Germanate



Ge

halogenl!I

cone. HN03



Germanium. will displace silver frOJ11 its solutions but will.

(10)not displace mer ury, tin. antiJD.ony or bismuth. Quanti-

copper.

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tative oxidation state relationships a.re shown below· in the poten­ tial diagram of Figure J.

Figure 3. Potential **Diagrams**

Acid Solution Alkaline Solution

o.o

Ge

+2 0\_.\_3-4

Ge02

1.0

Ge----

# 0.1 ;.

* 1. ·Compounds of Geru&ni'UI.II

Germanium, because of its position in the periodic table. is characterized by properties intermediate to those of silicon and

. tin below and above it. rmaniwn fo1"111s compounds in which the

oxidation states *ue* +2 and +4, the ger•anium (II) COIJPOUnds being less common th.an·those of **germanium** (IV). The +2 state is un- common in silicon and is on the other band more important in tin. This result is due to the fact that at::1mic size increases from

silicon to tin thereby reducing the ability ot the **atoms** to satu­ rate themselves covalently. Tin, thus, **is moat** likely to form an

•inert pair"·ion.: The smal.ler tendency of genumium· to form an

"inert pair".ion results in a positive two state even more strongly reducing in.character than divalent tin.

A brief discussion of the **more** important +2 and +4 compo nds of **germanium** follows:

The hydrous onoxid of **gernaniun** is amphoteric. rt is soluble

in acids and alkalis, reactioqs with the latter yielding solutions of germanites. The solutions in bydrohalic acids in which *the* ger­ manium is probably present in the form of halo complexes are rather st-able in the absence of oxidizing agents. The germanium (II)

on the other hand is converted to the-germanate ·ion anci hydrogen is evolved from highly alk;aline solutions.

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The genumium diha.lides are not -simp1e molecular compounds

as are the tetrahalides but appear to be pol}'lleric molecules in which the **germanium** atoms a.re bridged by halogens. They are un­ stable both toward hydrolysis and oxidation. Chloro"and iodo

c01111plexes **with the foraulas** MGeC13 **and MGeJ3 have** been prepared.

These are easily h\_ydroly?,ed **and a.re** '

·aiso readily oxidized

by **air.**

The **germanium** (II) sulfide· is·the most stable ger i1111 (Ir) cownpound **known and may** be melted and vaporized without decompo­ sition. It is slightly soluble in **water and** hydrolyzes rith th evolu\_tion of h-,drogen sulfide. It dis.solveli i\_n alkalis and in­ yellow **ammoni'IIII** sulfide.

Germanium dioxide is dimorphic, one \_modification possessing the quartz structure and the other the tetragonal rutile lattice, the latter form being stable below the transition teaperature of

10JJ0c.

Solutions of germanium dicxide are slightly acidic. At pH values of S.4 to 8.8 the principal ionic species is Ge5o11= (rather than eeo3•); the acid dissociation constant of H2ce5o11

is about 10-9. At pH Yalues above an4 below 8.4 to 8.8 lower stages of polymerization e ist.

Germanium. dioxide is amphotel).ic in• nature. Ontreatment with concentrated hydrofluoric or hydr\_ochloric acid conyersion to the volatile tetrabalide occ11rs. Dissolution in solutions

*of* **ai ali** yields germanates; meta-, M2Ge03 and ortho-germaoates.

M4Ge\_O4 a\_v be\_en reported.

The tetrahalides are volatile and tl:ieir thermal stability decreases from th tetrafluoride to he tetraiodide. ey are readily hydro\_ly?,ed. **Ger111aniu:n** forms bexahalo c\_omplexes with fiuorine and chlorine, the fluo complex GeP6• being rather

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stable in water whereas the analogous chloro **ioa is** rapidly hydro1yzed witb the precipitation of tbe dioxide.

* 1. Separation of Germauium Distillation of germaniu• tetrachloride is the standard

way of separating germanium from other elements. It can be easily sep rated from elements such as arsenic, tin, antimony, selenium and tellurium halides by virtue of its lower boiling temperature. A stream of chlorine to keep the arsenic in the no\_n-volatile quinquevalent state usures its complete remov:al from germanium.

nte distillate obtained from a hydrobrOlllic acid solution of a complex mixture such.as fission products rill, on the other

hand, contain arsenic and eleni'Wli as well a.s traces of tin and • antimony. The selenium present in the distillate can be remov d by precipitation with hydroxylaldne hydrochloride or with sulfur dioxide.

Also useful are the separations based on the use of hydrogen sulfide or alkaline sulfides. Germanium belongs with the elfwnts of fhe arsenic group of sulfides and can be precipitated.by hydrogen sulfide in acid s 1ution and separated from the copper group b\_ytreatment of the sulfide with alkaline sulfide or poly­

.sulfide.

Germanium .(IV) like tin (IV) forms a fluo **anion** in hydro­ fluoric acid solutions and can be separated fro• **stannous tin,** trivalent arsenic **and aatillODY, lelld-aud** copper which precipitate - with hydrogen sulfi e.

A problem to the radioche!ld.st is the incomplete precipita- tion am the·lll.most.co1loida1 form of the ge 111&niulll(IVJ sulfide(ll)

precipitate in acid solution. ni.e precipitated sulfide also

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teods to cause trouble vi th ordinary washing llll!diums and should be washed with six uorma.1 sulfuric acid that has been saturated with hydrogen suifide..

Separation of germani1111l from arsenic, galliu . zinc, copper, iron, **manganese, i,anadium,** titanium and zirconiWII bllt not molyb­ denum can be achieved by its precipitatiou wi-th a freshly prepared five percent·solution of tannin from chloride free eolutlon about one tenth normal. in sulfuric acid and three tenths mo·1ar in

a monimn. sulfate heated to about 95°C. Germanium is also pre­

cipitated quantitatively with tannin from oxa.tate solution at

*0.01* N acid.ity!12) The white precipitate that for111S settles qui\_ckly, is easily filtered and -shed. One precipitation\_ provides separation from vanadiu11, irconium, thorium, alu111:lnum and iron

1. ·The acidity is below t &t required f\_or tin and tantalum

but atiove that needed for **titanium..**

Ger'Cll&DiWII (IV) compound• are reduced by sodium hypophospbite in acid solution to the solobJ.e bivalent state while **areenic** compounds are reduced to·inso1uble elementary arsenic which can

then be remoYed by filtration.

'lb.e separation of germanium fron zinc can also be achieftd by aelectiYe reduction. In tbia case germa.niUJII is reduced to the metal fo:t:m with zinc duat.

Monogermaue can be reduced with bydro1en to deposit a rer­ maniwa mirror aimilar to that obtained in the Marah teat for ar&enic. Thia tec que :may be of potent.ia.l i111.portance to the radioebe:mist not ODly for separation purposes but also for·sample preparation. lb.e plating of ger.maldum **as a** thin uoiform fil.m by this method could eDha.ace the accurate measurement of weakly euergetic beta emitting nuclides of **germanium.**

Germanium (IV) chloride is quite insoluble in concentrated

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bytlrochloric acid (0 \_3 mg per IJr&m of acid at o0c.) aud can be

separated from soluble chlorides such•• arsenious, stannic and

\_titanic by **ah&ki'DI** with the acid in **a** separatory funnel. lbe chloride redissolves in fuming hydrochloric ·acid and is not

.reprec.ipitated from ether in t e event solvent extraction is employed for the separation of other chlorides.

Aromatic organic reagenta containing 2 phenol groups in ortho position.a **and a** group that is ortho or para to ol!e of them

. and capable of producing a prototropic system precipitate ger-

.mani WII.(l.3,l4,l5)

Por' eXU1.P1 e, 8'•11 ocyani

ne, tri

hyd roxyauri n,

pu.rpurogallin, 314 dihydro.xyazobe n and hem&toxylin are spe­ cific precipitating re&B:ents for geraauium. The minimwa ger­ manium concentration that is needed for its precipitation **as** insoluble complex from a one percent solution of these particular reagents in a hydrochloric acid-ethanol mixture is listed below together with the color of the product precipitate.

TABLE 3. PRECIPITATION OP GERMANIUM

Mini'lllUm Ge Cone.

Reagent (grams/cc. solution) Color of Precil)itate

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| GaJ.locyanine | 2 | X | 10-5 | dark violet |
| trihydroxyaurin | 3 | X | 10·1 | violet |
| purpurogallin | 1 | X | *10·3* | rose |
| 3,4 dihydro ya obeuzene | 4 | X | 10-5 | red |
| hel!latoxylin | 1.5x 10-6 red violet | | | |

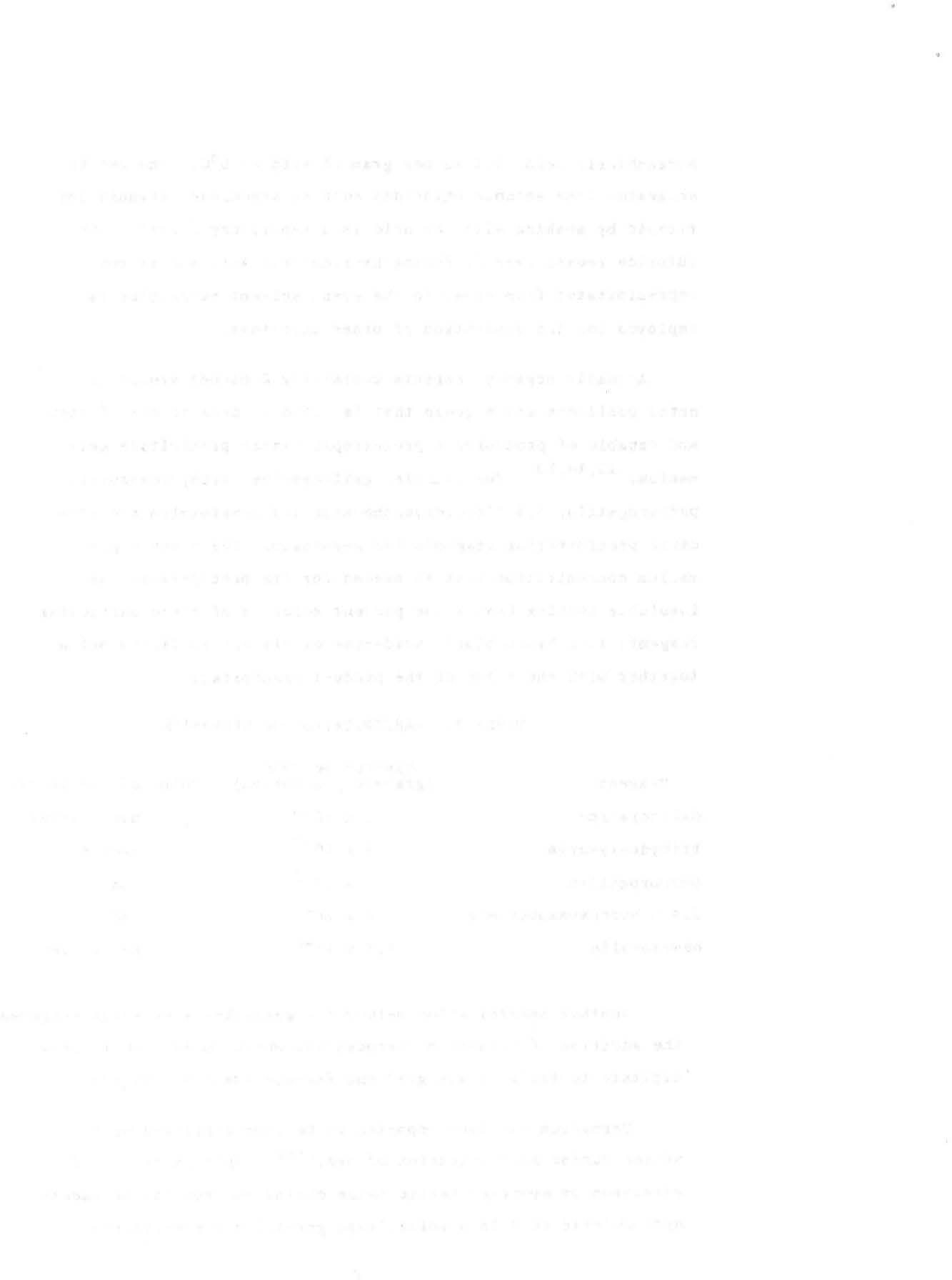
l\nother precipitation method for ger:maDilDI separation includes the addition of\_potassium ferrocyanide 11bich forms a white pre­ cipitate tentatively assigned the formul\_a(Ge0)2Fe(CN)6•2H20.

Germanium has been eporte4 to be coprecipitated with

sillca· during acid digesti'on of ore.<16>• coprecipitation of

germanium on hydrated ferric oxide during the remova.t or excess hydrochloric· acid in a volatilized germanium tetrachloride

* + lZ



. sample has been employed in the preparation of er111anium samples for colorimetric determi'Dation.<17) The.applicabi1ity of **these**

agents for pre1i:minary sepatation steps in the radiochemical isolation of germanium is apparent.

So1vent extraction techniques are employed importantly in the separation and deter:mination of germaniun, the solvent extraction of germaniu .(IV) chloride for further treatment being standard operating procedure. In a typical determination

the germanium, after guantitive remoYal as the tetrachloride from

concentrated hydrochloric acid into benzene(lS) or carbon tetra­ chloride<i9) is back-extracted into water for additional parifi-

cation.<20•21)

Separations **9-sed** on the extraction of **germani1Jll** (IV) halide intn **organic** solvents are of **special** utility to the radiocheaist. The difference in extraction behavior of Ge (IV)

and As (III) in hydriodic acid-chlorifor• systems is, for example, the'basis of **a** radiochemical sepuatiou of germanium a araenic.<22).

The.large difference in the distribution of Ge (IV) and As (III)

between CODCentrated hydrochlcnic acid solutiOJIS aat tile orprdc

solvents, carbon tetrachloride, ch1orfform, bia (2-cb1orethyl) ether am benzene has been employed for their separation also.(la)

Bxperilllentally determined distribution ratios for Ge {IV) am As (III) as a function of hydrochl.oric acid concentration and organic solvent(2J) are compared in Table 4 to show f:he large· difference in the extraction behavior of Ge (IV) and As (III)

at high hydrochioric aeid concentration values.

The removal of impurities from germanium by selective ex­ traction has received continuing attention. The separation of iron, a.nti1110ny, tin, arsenic, selenium and germanium by extrac­

tion with methyl iaobuty1 .Jcetoile from hydrochloric acid solution bas been investigated.<24> Tables *5* to·9 are presented to compa£e

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the extraction behavior of various elements with germ&DiWII iu severa.1 other systeu. **Genianiwa is** not appreeiably extrs.cted whereas many of the elelllent's are in most of "!he systems, that

are su.1U1arized in these tables. • This type of information may be •

employed usefully by tbe radiochenist.

TABLB 40 DISTRIBUTION RATIO VERSUS HYDROQiLORIC ACID OONCBN'nlAl'ION POR As CIII) AND Ge (iv> IN SBVERAL sOLOTIGNS AT Jo0c.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| ll)ldroahl.od.c  (f'orm vt/l.) | llla(2-ch1oro  e l.) **ether** | **Bensene** | **ChlorofOl'tl** | Clerbon Tetra-  obloride | IaoiroW1 |
|  | .!!. | !! |  | - ,!!!\_ | !!!. |
| ~2-.l | 0.020 o.01.2 | 0.0013 0,001. | 0,01'.ll **O.OQl** | 0.0006 O.OOJ.( | 0.13 o.oo, |
| -4-2 | 0,034 o.OJ.7 | . o.026 0.006 | o.oa3 0.01. | 0.00.5 0.003 | 1,3 0,078 |
| -6.3 | 0.63 0.027 | 0.23 0.17 | o.2li 0.35 | 0.24 0.076 | 17. 0,15 |
| ~ 8.3 | *96. 2.9* | '64. 4.5 | 1.25. 3.3 | ,,  125. 1.•.59 | b.2(). '1.32 |
| ~10.3  ~12,l. | 330- .1.2.5  309. J.3.0 | 2 - 17.7  434. 1.8.3 | 583. 6.9  630. 7.3 | 597'.. 3.7  59J+. 4 1 | 1L52. 0.30  w. ---- |

*s.* FUIORIIE D!IMC'l'IOBB

SQJ.wnt S,,.t.a {before 1111.x1ng)

Oxldll.t10;11, .Per Cent

El.enmnt State .Aqueoua l'taee Or-gan1c Pb&11e Extract1cD

AJ.U1111,uum

Antuoo;r

ASJIl.IImII))

20.M BJ' fthl'l. ether 0,2

.3,f M KP Btby'l. e . o.4

Sb Ill) ·20M!D' Rth;rl. ether 6.3

Sb V) ao:.M BJ' Et:byl. ether 0.1

.Areecic **Aa(II!}** li-.6 M HF Ethyl ..tner9- 62

As!m)

20 M BF 1 ether *31-1·*

As V) 20 **M** HF l. ether 13.6

:Beryllium *Be* zr• 20 M BF Btb1'1 etbar 4.o

Cadm:l.um

20M Etll.Y;L ether. l..4

Chrom:l.um er III) 20**MD'** Btb,yl. etber <0.1

ca.In

Cobe.J.t Coll) 29MD' Bt'.h;yl. et.lier :i..7

Co CU II) **a>MHI'** B:t21yl. ether 1.3

Ge.ll.iUDI Ga Ill) . 20M BF . Bth;rl. e:t;her <0.05

Ge.n!Janj,wa ame mIV)) 20·M BF' .Btb.Yl. ether *'6,7 •*

IndiWII

20 M BF l. etber <0.05

Iron Fe ll) 20**M**BY l.fll:bar <0,1

:119 Ill) 2.0 MBP lether <O.l.

Mllnpneae Mn(II) 20 M !IF Etb;71 ether l..3

Mercury· Hs(ll.) 20 **M Bll'** JltbTl. ether 2.7

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5, (Continued)

Sol.vent Syll"tem (befoN lllizlq)

Oxid&tion Pi:tr Cent

Element Sta.ta AqueQlla Phase ()rp.nl.c **l'ti&N** kti'aot1on

liblybdenum .MD(Yr) 10 M HP'• 6 M !Ji3011;• Hatll;rl 1 but;rl 9.7

2,2 **ll** D1i,P ntone

lib('VI) 3.5M BJ' l **etmr5** 9.1

l&l(VIj 20 MD Etql. ether 9.3

Nickel Ni I:I 20 MHF Btll;rl ether 0.7

N:1.cbium 9MBF., 6 **M -** D11eo.pl'OPY1 )ratom,b

Bb(V 6 M HP'., 6 **M** D11110b 1cm-b1Dolb

llb(V) 1.0 M RP., 6 M fi., Mlt l. 1sobut71- 96

2 •.2 **M** BB!i.F ketoil.eb

lib v

11b(V) 20. M BJ' Etllyl etaer

Phqephorue • l'(V) 20 **M** ID' Btql ether

i;3.

65.8

14,8

Protactinium Pa(V) 8 K·BCJ.\_, 0.6 MU, 1111.t. D11ao»ropyl. uto.cie 100

AlCl.

Rhem.ma k{VIl) 20M l• 61.8.

: 20 MBJ' .Bt!Q-1 **etber** 12.9

SeJ.euium Sa(IV} 4.6 M BJ' :llt;ql eiibe - 3.1.

Silicon 20 BI' EthTl etber <O,l

Silver 20MB7 EtbTl. ether 0.05

Ac I)

T!mtal.1mf **Ta** V) l.O **M BP.,** 6 M.¥04 Mlrtlr.11 iaobutyl 99.6

\_2.2 **M** Jratoneb

:i!}

0 4 **)l BJ'•** 3, 7 **N** HCl. D1iaoJ7,l'OPYl **b-** 8.t. '.DI/Hb.:91.)

0.4 M111', •3,9 M BJI D11aoprapyl lreto119 79 /Jlb..88o)

0,4 M JII', 4.5 **M** lif2S 4 l>iiaop:rop,11 ketoneb 95 /lb=l.60)

Ta V) 0,4 K 111' 4.6 **M** ECi04 Diii,opropyl ketoneb *90* /lb.:290)

Ta V) 20 M BJ' let.her 79 3

Tellurium Te :tV) 20 **M BJ'** l etber 2.3

'l!lal.l.iUll! r) 20MB lttJJ,yl ether <(),05

Tin Sll(ll) IJ.,6 M BF lother"- 100

Sn(II) 20 M BF Btll;rl. other 4.9

**BniIV)** l.,2.J+.,6 M l!P Etll;rl et.bet" 100

Sn IV) 20 M HJ' l ether 5.2

Titanilllll Ti(IV) 20MllF .Rtlo"l. etber <O.O, Tun«ate.n. W(VI) lOM:e:F.6M S04, Metll;rl iaob'il"Qtl -26

2■2 M llf4F **btoneb**

20 M BF Jtt.h7l•. **ether** 0.5

Uran:1.um

! !il

20 **M** HP' .Et.b;Tl **et.her.** J..l.

VaDll-dium V(Ill) 20M:a:F Bthy-1 lfl:ber l2

V(V) 20 M Hll' l. ether 8.5

Zina Zi ll) 20MBl!' l. 0.9

Zirconium zr IV) 20 M llF Ji:t:ql ether 2.9

84:J.vol.ume ratio ar- orpm.c to aqueous pi&ae,

b0rgam.c pb.aae pre..eqUU1l;)rated nth pure **aque0118 pbaae.**

15

.,