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Au, Ag, Bi, Br, Cd, Cs, Ge, In, Ir, Ni, Os, Pd, Rb, Re, Sb, Se, Sn, Te, Tl, U, and Zn as well as Sc, Y, and REE

by

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FOREWORD

The Committee on Nuclear and Radiochemistry is one of a number of committees working under the Board on Chemical Sciences and Technology of the Commission on Physical Sciences, Mathematics, and Resources of the National Academy of Sciences--National Research Council. Its members are drawn from academic, industrial, and government laboratories and represent the areas of nuclear chemistry, radiochemistry, and nuclear medicine.

The Committee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, specialized techniques and instrumentation, the place of nuclear and radiochemistry in college and university programs, the training of nuclear and radiochemists, radiochemistry in environmental science, and radionuclides in nuclear medicine. A major interest of the Committee is the publication of the Nuclear Science Series of monographs on Radiochemistry and on Radiochemical Techniques. In 1982 a third series on Nuclear Medicine was initiated.

The Committee has endeavored to present monographs that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique or with the use of radionuclides in nuclear medicine.

Experts in the various subjects have been recruited to write the monographs. The U.S. Department of Energy sponsors the printing of the series.

The current monograph is one of the series on Radiochemical Techniques which grew out of the need for compilations of specialized techniques and instrumentation in this field. The Committee is confident these publications will be useful not only to nuclear and radiochemists but also to research workers in other fields such as physics, biochemistry, or nuclear medicine who wish to use radiochemical techniques to solve specific problems.

Edward S. Macias, Chairman
Committee on Nuclear and Radiochemistry

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INTRODUCTION

RAISON D'ÊTRE AND OVERVIEW

In lunar and terrestrial rocks and in meteorites, the radiochemical neutron activation method described here enables determination of the 21 trace and ultratrace elements Ag, Au, Bi, Br, Cd, Cs, Ga, Ge, In, Ir, Ni, Os, Pd, Rb, Re, Sb, Se, Te, Tl, U, Zn, as well as 13 rare earth elements (REE), Sc and Y.

The Apollo lunar sample program stimulated the initial development of this analytical procedure. Previous work on meteorites had focussed interest on two groups of trace elements - siderophiles and volatiles - and these were expected to elucidate both the Moon's origin and its history of meteorite bombardment. In the 1960's these elements in meteorites were generally measured a few (1 to 4) at a time. The imminence of the lunar program provided an incentive to develop multi-element procedures, both to conserve rare material and to permit more precise determination of interelement ratios. For many (mainly lithophile) elements, instrumental neutron activation analysis (INAA) was satisfactory, but for most of the siderophile and volatile elements - with abundances in the range of 10^{-9} to 10^{-12} $g.g^{-1}$ - only radiochemical analysis (RNAA) possessed the required sensitivity and precision. Accordingly, a comprehensive scheme for the simultaneous determination of up to 20 elements was developed at Chicago, starting in 1968 (Keays *et al.*, 1974). The method proved extremely useful for many studies other than lunar (Morgan, 1977). More elements of interest were added without changing the basic structure (Gros *et al.*, 1976). Availability of high resolution solid state detectors relaxed the requirement of ultimate radiochemical purity for those radionuclides with useful gamma- or X-ray lines. Although the procedure worked well and was used to analyze several hundreds of lunar, meteoritic and terrestrial samples, it was laborious, requiring 3 or 4 chemists in the early stages to recover the shorter-lived radionuclides. Also, the separations had become convoluted due to grafting on of additional elements. The procedure therefore was systematically redesigned between 1977 and 1979. Where possible, precipitation and solvent extraction procedures were replaced by ion exchange steps that were themselves thoroughly optimized to give expeditiously higher yields and more rigorous decontamination. The new procedure as described below may be applied to up to 16 samples (including controls) by two chemists with some part-time assistance during the first few days. Using a thermal neutron flux of 10^{14} n.cm^{-2} sec^{-1} or better, sensitivities fall in the following ranges (in ng):

10^{2} - 10^{1}	Ni
10^{1} - 10^{0}	Rb
10^{0} - 10^{-1}	Br
10^{-1} - 10^{-2}	Cs, Ga, Se, Te, U, Zn
10^{-2} - 10^{-3}	Ag, Bi, Cd, Ge, In, Pd, Sb, Tl
10^{-3} - 10^{-4}	Au, Ir, Os
10^{-4} - 10^{-5}	Re

Radiochemical yields are generally determined gravimetrically for the 15 elements having suitable stoichiometric precipitates; for the remainder, recoveries are assayed by re-irradiation or, in the case of Cs and Rb, by addition of Cs^{137} radioactive tracer.

The precision of the method is generally 10% or better for abundances well above the limit of detection with reasonably homogeneous samples (as shown for example in Morgan, 1977). In favorable cases, as with the H-chondrite work described in a later section, the precision has allowed differences in elemental ratios as small as 5 to 10% to be demonstrated (Morgan *et al.*, 1985). The results of replicate analyses listed below give an idea of the precision that may realistically be expected:

	Orgueil(a)		Allende(b)		BCR-1(c)	
	mean	σ(%)	mean	σ(%)	mean	σ(%)
Re	38 ppb	11	68 ppb	8	0.82 ppb	5
Os	532 ppb	9	833 ppb	8	≤ 2 ppt	
Ir	466 ppb	5	776 ppb	5	1.7 ppt	35
Pt	920 ppb	7				
Pd	535 ppb	9	705 ppb	12	≤ 0.2 ppb	
Ni	1.10%	5	1.42%	5	9 ppm	11
Au	136 ppb	19	137 ppb	7	0.52 ppb	30
Sb	182 ppb	16	74 ppb	7	565 ppb	8
Ge	32.4 ppm	4	15.3 ppm	15	1.52 ppm	6
Ag	223 ppb	11	91 ppb	2	24 ppb	4
Se	18.0 ppb	3	8.1 ppm	7	79 ppb	3
Te	2.2 ppm	4	0.96 ppm	5	5 ppb	31
Zn	303 ppm	3	113 ppm	1	131 ppm	3
Sn	1.71 ppm	11				
Br	3.6 ppm	16	1.52 ppm	3	56 ppb	9
In	74 ppb	5	30 ppb	50	93 ppb	7
Cd	711 ppb	6	474 ppb	2	139 ppb	7
Bi	103 ppb	14	45 ppb	4	45 ppb	3
Tl	151 ppb	5	59 ppb	2	280 ppb	3
Rb	1.93 ppm	19	1.04 ppm	8	47 ppm	5
Cs	183 ppb	3	92 ppb	15	958 ppb	6
U			14 ppb	9		

a) New data of Ebihara et al. 1982, based on 4 replicate analyses.

b) Data summarized by Takahashi et al. 1978, based on up to 6 replicate analyses.

c) Controls run since Keays et al. 1974, based on 15 replicate analyses; 12 at Chicago and 3 at USGS, Reston.

CHOICE OF ELEMENTS

In designing this procedure, elements were chosen primarily to inform about planetary processes or fractionation in the early solar system; ease of analysis was a secondary issue. This represents a fundamental difference from the widely-used INAA technique, where the suite of elements is governed chiefly by the presence of prominent photopeaks and less by the problems to be solved. For the most part, the elements selected for RNAA are not accessible by INAA. [Nonetheless, a preliminary INAA before RNAA on the same sample provides useful complementary information.]

Volatile elements

Volatility, in the present context, refers to condensation temperature from a cooling gas of solar composition (predominantly H_2) as calculated from thermodynamics (Grossman and Larimer, 1974; Wasson, 1985). The highly volatile elements have condensation temperatures for pressures about 10^{-5} atm. between 400 and 500K and include Tl, Cd, Bi, In, Pb (and Cs?). These elements are very variable in chondritic meteorites and are potentially useful cosmothermometers. Lead was not included in the present suite of elements because of poor neutron activation sensitivity. A second group of moderately volatile elements condenses in a range between 600 and 1100 K (just after the condensation of metallic FeNi at 1200-1300 K). This group comprises such elements as Zn, Se, Te, Br, Ga, Rb; the siderophile elements Ge and Sb also condense within this temperature range. The moderately volatile elements characteristically tend to be depleted as a group in any given planetary body or meteorite; and in chondrites they show significantly less variability than the highly volatile elements.

Siderophile elements

Elements characterized as siderophiles condense as free metals, and therefore end up in the most abundant metal phase, FeNi, regardless of condensation temperature. Thus, siderophile elements cover a wide range of condensation temperature and may be crudely divided into three groups on this basis, depending on whether they come out of a cooling gas phase before, simultaneously with, or after metallic FeNi. The refractory siderophile elements analyzed include Os, Re, and Ir; Ru, with a condensation temperature similar to Ir, could be added in principle, but in lunar samples of low Ru content, the Ru activity from U fission becomes troublesome. The "normal" siderophiles accompanying metallic Fe during condensation include Rh, Ni, Co, Pd, and Au. Because of the very short half-life of the nuclides produced by neutron activation, Rh was not included in the suite of elements. Cobalt, formerly included in our RNAA procedure (Keays *et al.*, 1974), may be determined conveniently by INAA if required. It is not as siderophile as the other elements listed, however, and for many purposes is less informative. The volatile siderophile elements condensing after Fe include Ge and Sb, with condensation temperatures corresponding to the "moderately volatile" non-siderophile elements discussed above.

Incompatible elements

These elements do not fit easily into the lattice of many rock-forming minerals, either because of high ionic charge, as in the case of U, or large ionic size, as with Rb and Cs. These elements are sensitive indicators of igneous fractionation processes and were therefore included in the RNAA procedure; they are particularly useful when used with REE and other data. As mentioned earlier, REE can be included in the RNAA procedure for levels beyond the sensitivity of INAA. Detailed methods for REE are available elsewhere (Laul, 1979; Wandless and Morgan, 1985). The present procedure describes step-by-step separations only for the first 21 elements listed in the title.

APPLICATIONS

Solid solar system material has undergone one or more of the following processes: condensation and accretion from the solar nebula; large scale planetary differentiation, including separation of a FeNi metal core; magma formation by partial melting of planetary mantle; igneous emplacement and fractionation by crystallization; modification by weathering, metamorphism, recycling, impact, etc. An important part of any study is to determine which of these processes apply to the subject material, and how they affected it.

Chondrites

These meteorites are the most abundant type seen to fall and are the least fractionated, having undergone only superficial changes since formation 4.6 x10^9 years ago. The name is derived from millimeter-sized globules of silicate called chondrules that all except one chondrite class contain.

Cosmic abundances

Many lines of evidence converge to indicate that the C1 chondrites are the most primitive, least fractionated chondrite class. Unlike other chondrites, they contain no chondrules, but are rich in volatiles, organics and H_2O. Analysis of several different specimens of the 3 available C1 falls (Krähenbühl *et al.*, 1973; Ebihara *et al.*, 1982) combined with known isotopic abundances has pinned down important areas of the cosmic nuclide abundance curve. In combination with critically evaluated literature values for other elements, these data have provided the basis for a revised cosmic abundance table (Anders and Ebihara, 1982). Cosmic abundances are of importance to nucleosynthetic models, and provide a valuable baseline for understanding cosmochemical and planetary fractionation.

Carbonaceous chondrites

The fine structure of trace element patterns reveals no evidence of nebular fractionation in C1 chondrites. Hydrothermal transport on scales between cm and km may be responsible, however, for internal abundance variations of a few elements such as Br (Ebihara *et al.*, 1982). Nonetheless, the C1 chondrites remain the best available sample of unfractionated solid solar system material. Other C-chondrites show progressively less aqueous alteration, increasing presence of high temperature minerals (principally in the form of chondrules) and are divided on this basis into C2, C3 (and C4) types. Most C2 chondrites are denoted C2M (after Mighei, the type specimen); they contain about 50% chondrules in a fine-grained volatile-rich matrix. The trace element pattern reflects this. Elements with high condensation temperatures (>1200 K) show no depletion, but volatile elements (<800 K) are uniformly depleted by a factor of 0.48, a value close to the planimetrically-determined matrix content of 0.50 (Wolf *et al.*, 1980). The C3 chondrites fall chiefly into Vigarano (C3V) and Ornans (C3O) groups. Volatile elements are depleted by a factor of 0.25 - more than would be expected from matrix content (0.43 in C3V and 0.37 in C3O) (Anders *et al*. 1976; Takahashi *et al.*, 1978). Apparently the C3 matrix received variable amounts of volatile elements due to dust-gas fractionation in the solar nebula.

H-Group chondrites

Precise siderophile analyses demonstrate conclusively that the petrological types H3 to H6 (numbers increasing with degree of metamorphism) do not form an isochemical metamorphic series; rather, the H3's are depleted relative to other types by 10% not only in Fe but also in the siderophile elements Os, Re, Ir, Ni, Au, and Pd (Morgan *et al.*, 1985). The highly volatile elements Cs, Br, Bi, Tl, In, Cd decrease in abundance by $\approx 10^{-3}$ passing from H3 to H6, as also shown for L-chondrites (Keays et al., 1971). The trends do not resemble those expected for metamorphic loss, but appear to be a primary feature derived from nebular condensation, perhaps with gas-dust fractionation.

Enstatite chondrites

Enstatite chondrites, like other chondrites, are apparently nebular condensates; but their highly reduced nature suggests unique conditions in the region of the solar nebula where they formed. These meteorites are divided into a high-iron (EH) group, comprising the E4's and a low-iron (EL) group consisting of E5's and E6's. The EL and EH groups contain similar amounts of refractory siderophiles Re, Os, Ir at approximately C1 levels, suggesting that both groups received a full complement of high-temperature early condensate. For elements more volatile than Ni, however, the EL group has abundances consistently lower than EH; the difference increases with element volatility (Hertogen *et al.*, 1983). The distribution of volatile elements agrees well with that expected from metamorphism, judging from heating experiments (Binz *et al.*, 1974). A similar comparison with condensation is hampered by the lack of thermodynamic data for the unusual trace element host phases in enstatite chondrites.

Achondrites

Unlike the chondrites that are thought to be nebular condensates, the achondrites appear to have formed on parent bodies by igneous differentiation of primitive chondrite-like material. In particular, the achondrites themselves tend to be low in Fe-Ni metal and siderophile elements, even though associated occasionally as breccias with massive meteoritic iron.

Eucrites and diogenites

These achondrites are unequivocally igneous in origin, though most specimens have suffered subsequent impact brecciation. The frequent occurrence of eucrites and diogenites intimately mixed in impact breccias (howardites) suggests, along with other lines of evidence, that these meteorites were derived from the same parent body. Similarities in trace element distribution support this view. The trace element pattern strongly reflects planetary differentiation, showing severely depleted siderophile element abundances as a result of core formation of the parent body (which may be the asteroid Vesta). Abundances of volatile elements (Rb, Cs, Br, Bi, Tl) relative to such refractory elements as REE and U are very low, suggesting that the eucrite parent body is as volatile-poor as the Moon (Morgan *et al.*, 1978; Wolf *et al.*, 1983).

Aubrites

These enstatite achondrites are undoubtedly related to the E-chondrites as illustrated by similarities in mineralogy and a common unique oxygen isotope signature. It has been suggested that the aubrites may actually be nebular condensates rather than igneous differentiates but trace element data suggest otherwise. The siderophile elements pattern is typically that resulting from planetary differentiation; correlation between volatile and non-volatile siderophile elements indicate that the overall siderophile depletion results from metal separation rather than incomplete condensation (Wolf *et al.*, 1983). The low ratio of volatile to non-volatile lithophile elements suggests that aubrites may have been derived by igneous processes from parental material resembling the EL chondrites.

Ureilites

These unusual meteorites consist predominantly of olivine and clinopyroxene of cumulate origin, shot through with carbon-rich veins containing Fe-Ni metal and shock-induced diamonds. Analysis of bulk ureilites (Higuchi *et al.*, 1976) and vein separates (Janssens *et al.*, 1987) shows that the siderophile and volatile elements occur predominantly in the vein material, which possesses a metal phase with an unusually high (Os, Ir, Re)/Ni ratio; a second metal phase, poor in Os, Ir, Re is associated with the ultramafic rock. The high Os, Re, Ir in vein metal is accompanied by high Ge, a volatile siderophile element; thus the trace siderophile pattern is not due to nebular condensation but to fractional crystallization of metal. The volatile element pattern suggests that the ureilites formed by a multistage process from material akin to C3V chondrites.

The Moon

The Moon's crust is predominantly composed of the light-colored anorthosite of the highlands and the dark mare basalts. Comparison of these igneous rock types with analogous terrestrial and meteoritic rocks can place tight constraints on lunar composition. Not all lunar rocks are igneous, however. To a far greater extent than on Earth, lunar geology has been determined by impact processes, the products of which include melt rocks, breccias and the comminuted lunar soil.

Igneous rocks

Lunar mare basalts and fresh terrestrial ocean ridge basalt glasses (Hertogen *et al.*, 1980) have essentially identical volatile trace element patterns, suggesting that both bodies assumed their volatile content from a similar source, and that the Moon is not the product of some cosmically unique event (Wolf *et al.*, 1980). The lunar basalts are lower in average volatile content by a factor of 0.026, however, indicating that the Moon acquired significantly less volatile-rich component than did the Earth. Marked siderophile depletion in mare basalts relative to terrestrial analogues reflects the low f_{O_2} in the lunar source region and the secondary enrichment of the Earth's mantle in these elements (Kimura *et al.*, 1974; Morgan, 1986).

Comparison of lunar highland anorthosites with Ca-rich anorthosites from the layered Fiskenaesset, Greenland complex shows surprisingly uniform volatile contents (when normalized to C1-chondrites); again with the lunar rocks showing a relative depletion similar to that seen in basalts (Morgan *et al.*, 1976).

Impact breccias

The lunar highlands are predominantly composed of melt-rich breccias chiefly derived from basin-forming collisions and large cratering impacts in the first 600-700 m.y. of the Moon's history. Siderophile and volatile elements in the breccias reveal characteristic patterns with selenographic groupings that seem to be associated with specific large impacts (Hertogen *et al.*, 1977). The composition of the colliding planetesimals shows a secular trend in which the most "moon-like" volatile-poor bodies fell earliest and compositions became increasingly refractory-poor with time. This sequence may reflect the sweep-up of moonlets in Earth orbit during tidal recession of the Moon.

Lunar soils

The continuous comminution of the lunar surface by impacts in many size ranges leads to a uniform covering of finely-divided material. In mare regions, where the target rocks are basalts low in siderophile and volatile elements, the enrichment of these elements seems largely due to a constant rain of micrometeorites. The siderophile-volatile pattern approximates that of C1 chondrites, and abundances reach a saturation level of 1.5 to 2.5% C1; this component may be of cometary origin (Morgan *et al.*, 1977).

Earth

Terrestrial studies based on siderophile and volatile trace elements have focused on three topics: comparison of basalts and anorthosites with lunar and meteoritic analogues, as discussed above; abundances in ultramafic xenoliths and in the upper mantle; and, characterization of bodies responsible for large impact craters.

Ultramafic nodules

The upper mantle is sampled by nodules (or xenoliths) of peridotite that are brought to the surface in kimberlite diamond pipes or in basaltic eruptions. The accretionary history of the mantle is hinted at by inferred mantle abundances, which fall into three groups (Morgan and Wandless, 1979; Morgan *et al*., 1980, 1981; Morgan, 1986); highly siderophile elements (Os, Re, Ir, Pd, Au, Re) 0.007 x Cl and chalcogens (S, Se, Te) 0.003 x Cl; moderately siderophile elements (Ni, Co) 0.2 x Cl and (Ge) 0.03 x Cl; and volatile elements (Zn) 0.2 x Cl, (other volatile elements are lower). Although the highly siderophile elements in the mantle are markedly depleted relative to chondrites, their abundances are about 10^3 times larger than expected for silicate in equilibrium with a metal phase. The moderately siderophile elements are less depleted, and their ratio to highly siderophile elements, exemplified by Ni/Ir, is much higher than the range in chondrites, suggesting some unusual fractionation process during core formation. In addition, the low ratio of Ge (a volatile moderately siderophile element) to Ni and Co indicates a volatile-poor source for these elements. The following scenario explains these (and other) observations, but perhaps not uniquely. Apparently the Earth initially accreted from volatile-poor, chondrite-like material that was sufficiently reduced for Ni, Co, Ge and the highly siderophile elements to be entirely in a disseminated metal phase. At later stages, more oxidized carbonaceous material accreted, introducing increasing amounts of volatile elements. Concomitantly, partial oxidation of metal released some 20% of Ni and Co from the metal to the silicate phases, while about 80% of these elements and all of the highly siderophile elements remained in relict metal. Core formation removed metal and sulfide (since Fe-Ni and FeS form a low melting point eutectic), completely stripping the mantle of highly siderophile elements and chalcogens and also removing 80% of Ni and Co. A late influx of planetesimals of chondritic composition during the first 600 m.y. of Earth's history, consistent with that observed on the Moon, introduced the present mantle abundances of the highly siderophile elements and chalcogens.

Impact craters

Because of the atmosphere and plate tectonics, impact geology may be less important, and is certainly less visible, on Earth than on the Moon. Large (>1 km dia) terrestrial impact craters of widely varying ages and sizes do exist, however, and in some cases, the projectile can be identified from its chemical "signature". Such studies provide "ground truth" for lunar crater investigations, and offer insight concerning the composition of large objects not represented in museum meteorite collections.

Nevertheless, high terrestrial crustal levels of siderophile and volatile elements make the characterization of the impactor more difficult on Earth than on the Moon. In addition, under oxidizing terrestrial conditions, such elements as Re, Se, and Ge may be lost by volatilization during impact, and by weathering at very old craters. Extensive studies lead to the following conclusions (Morgan *et al.*, 1975, 1979; Palme *et al.*, 1979, 1981; Janssens *et al.*, 1980; Wolf *et al.*, 1980; Morgan and Wandless, 1983). At craters where discrete samples of the projectile exist (e.g., Wabar and Meteor

Crater), their trace element signatures match those in crater ejecta, confirming the validity of the method. Elsewhere, a meteoritic signature is most commonly found in the melt rock sheet, when this is accessible. Such studies resolved a long-standing paradox: whenever meteorite fragments are found at a crater invariably they are irons (or stony irons), although among observed falls irons are outnumbered by stones 13:1. This inbalance began to disappear when craters lacking meteorite fragments were examined for chemical traces of the projectile; several appear to have been made by stones, both chondrites and achondrites. The absence of stone meteorite fragments at craters seems to reflect merely their faster weathering rate and low crushing strength.

NUCLEAR DATA

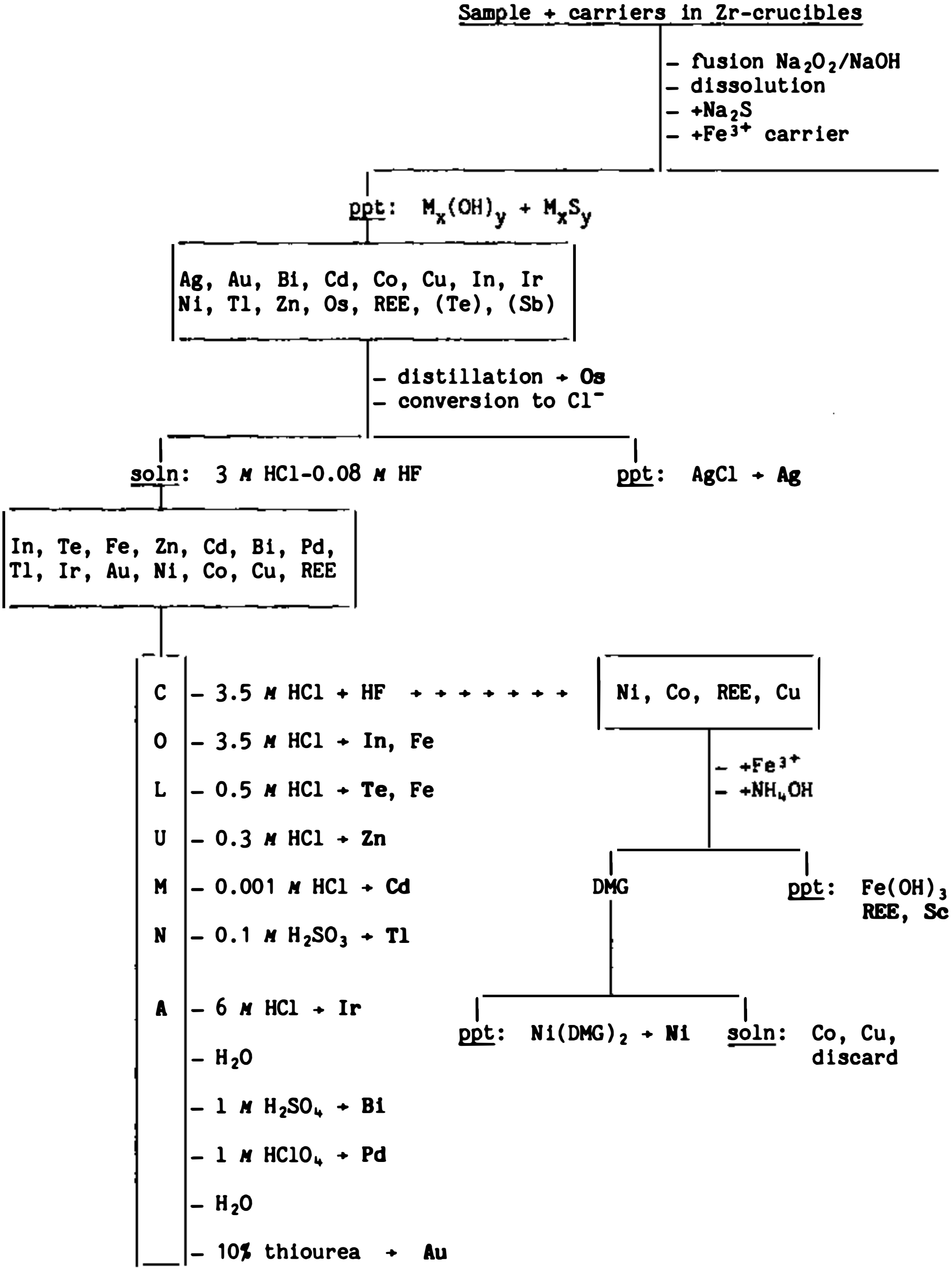
The relevant data for the 21 principal elements measured in this procedure are given in Table 1. The most likely interferences are also listed.

IRRADIATION

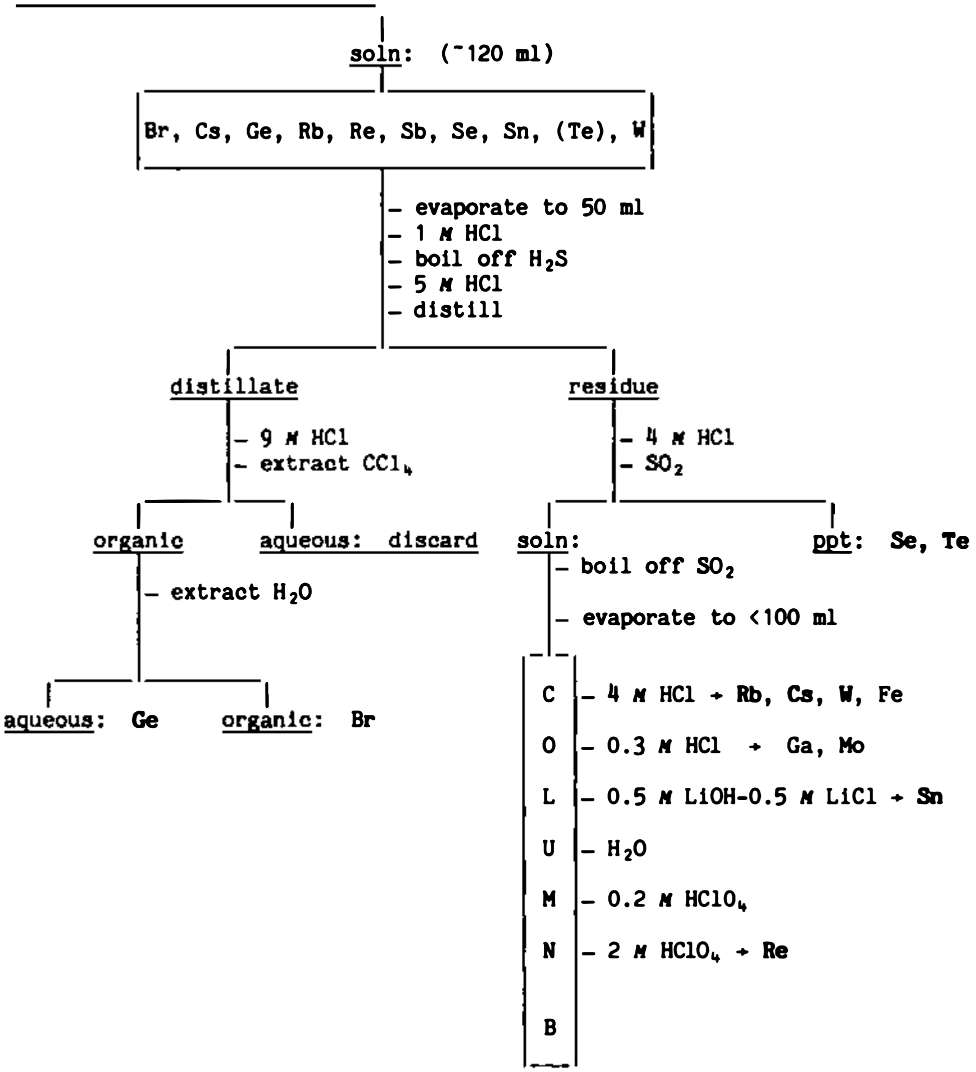
Irradiations are made in batches generally consisting of 12 samples with appropriate standards; more samples (up to 17) are irradiated when fewer elements are sought. Number 12 or 17 always is a reference sample of known composition, such as Columbia River Basalt BCR-1, or Allende C3V chondrite (standard sample of U.S. National Museum). For sample sets of very diverse composition, both standards are included. Most runs use the National Bureau of Standards reactor in Washington, D.C., which yields a dose of ~2 x 10^{20} n in a 10-day irradiation. Samples containing high abundances of these elements, (e.g., chondritic meteorites) are irradiated for shorter periods at a lower-flux reactor (5 x 10^{13} n/cm^2 sec.).

Table 1. Nuclear Data

Stable Isotope (% abundance)	Cross Section barns	Isotope produced	Half-life (decay mode)	γ-energy (keV) (% abundance)	Interferences
Au^{197} *(100)*	98.8	Au^{198}	2.696 d (β^-)	411.8 *(95%)*	Hg^{198} *(n,p)*
Ag^{109} *(48.65)*	3.2	$\mathrm{Ag}^{110\blacksquare}$	252 d (β^-)	657.6 *(96%)*	Cd^{110} *(n,p)*
					In^{113} *(n,α)*
Bi^{209} *(100)*	0.015	Bi^{210}	5.01 d (β^-)	---	-- --
Br^{81} *(49.46)*	3.26	Br^{82}	35.34 h (β^-)	554.2 *(66%)*	Kr^{82} *(n,p)*
				619.0 *(41%)*	Rb^{85} *(n,α)*
Cd^{114} *(28.86)*	1.1	Cd^{115}	53.4 h (β^-)	335.0 *($\mathrm{In}^{115\blacksquare}$, 4.5h)*	U^{235} *(n,f)*
				527.7 *(26%)*	
	0.14	$\mathrm{Cd}^{115\blacksquare}$	44.8 (β^-)	934.1 *(1.9%)*	In^{115} *(n,p)*
				1289.9 *(0.9%)*	Sn^{118} *(n,α)*
Cs^{133} *(100)*	30	Cs^{134}	2.062 y (β^-)	796 *(88%)*-802 *(7%)*	Ba^{134} *(n,p)*
Ge^{70} *(20.55)*	3.2	Ge^{71}	11.2 d (EC)	Ga x-ray	Se^{74} *(n,α)*
In^{113} *(4.23)*	8.0	$\mathrm{In}^{114\blacksquare}$	49.51 d (IT,EC)	190.2 *(17%)*,558.2,725.1	Sn^{114} *(n,p)*
Ir^{191} *(37.3)*	910	Ir^{192}	74.2 d (β^-)	316.5 *(81%)*	-- --
				468 *(49%)*	-- --
Ni^{58} *(67.76)*	4.4	Ni^{59}	$7.5\mathrm{x}10^4$ y (EC)	Co x-ray	-- --
Os^{190} *(26.4)*	4	Os^{191}	15.4 d (β^-)	129.4 *(25%)*	-- --
Pd^{102} *(0.96)*	4.8	Pd^{103}	17.0 d (EC)	Rh x-ray	-- --
Rb^{85} *(72.15)*	0.9	Rb^{86}	18.8 d (β^-)	1076.6 *(8.8%)*	Sr^{86} *(n,p)*
					Y^{89} *(n,α)*
Re^{185} *(37.07)*	105	Re^{186}	90.6 h (β^-)	137 *(9%)*	Os^{186} *(n,p)*
Sb^{123} *(42.75)*	3.3	Sb^{124}	60.2 d (β^-)	602.7 *(97%)*	Te^{124} *(n,p)*
				1691 *(50%)*	I^{127} *(n,α)*
Se^{74} *(0.87)*	30	Se^{75}	118.5 d (EC)	136 *(57%)*	Kr^{78} *(n,α)*
				264.6 *(60%)*	
Sn^{112} *(0.96)*	1.2	Sn^{113}	115.1 d (EC)	391.7 *($\mathrm{In}^{113\blacksquare}$, 1.6h)*	-- --
Sn^{116} *(14.2)*	0.006	$\mathrm{Sn}^{117\blacksquare}$	14.0 d (IT)	158.4 *(83%)*	Te^{120} *(n,α)*
Te^{122} *(2.46)*	1.0	$\mathrm{Te}^{123\blacksquare}$	119.7 d (IT)	158.8 *(84%)*	Xe^{126} *(n,α)*
Tl^{203} *(29.5)*	11	Tl^{204}	3.77 y (β^-)	Hg x-rays	Pb^{204} *(n,p)*
U^{235} *(0.72)*	579 *(n,f)*	Te^{132}	78 h (β^-)	230 *(0%)*	-- --
W^{180} *(0.13)*	10	W^{181}	121 d (EC)	Ta x-rays	-- --
Zn^{64} *(48.89)*	0.82	Zn^{65}	244.1 d (EC)	1115 *(49%)*	-- --


Sample + carriers in Zr-crucibles
– fusion $Na_2O_2/NaOH$
– dissolution
– $+Na_2S$
– $+Fe^{3+}$ carrier
ppt: $M_x(OH)_y + M_xS_y$
Ag, Au, Bi, Cd, Co, Cu, In, Ir
Ni, Tl, Zn, Os, REE, (Te), (Sb)
– distillation → Os
– conversion to Cl^-
soln: 3 M HCl-0.08 M HF
ppt: AgCl → Ag
In, Te, Fe, Zn, Cd, Bi, Pd,
Tl, Ir, Au, Ni, Co, Cu, REE
C
O
L
U
M
N
A
– 3.5 M HCl + HF → → → → → → →
Ni, Co, REE, Cu
– 3.5 M HCl → In, Fe
– 0.5 M HCl → Te, Fe
– 0.3 M HCl → Zn
– 0.001 M HCl → Cd
– 0.1 M H_2SO_3 → Tl
– 6 M HCl → Ir
– H_2O
– 1 M H_2SO_4 → Bi
– 1 M $HClO_4$ → Pd
– H_2O
– 10% thiourea → Au
– $+Fe^{3+}$
– $+NH_4OH$
DMG
ppt: $Fe(OH)_3$
REE, Sc
ppt: $Ni(DMG)_2$ → Ni
soln: Co, Cu,
discard

Flow Chart



Flow Chart (continued)

In some cases (Br, Ge, Ir, Rb) chemical yields are measured by reactivation, using a 10 min. irradiation at 10^{12} - 10^{13} n/cm^2 sec and taking appropriate care to avoid or correct for flux gradient and self shielding.

OUTLINE OF CHEMICAL PROCEDURE

After irradiation, samples are fused in the presence of carriers in Zr crucibles, using a Na_2O_2-NaOH mixture. The fusion cake is dissolved in water and Na_2S added. The separations are outlined in the preceding flow chart.

The precipitate of mixed hydroxides and sulfides contains Ag, Au, Bi, Cd, In, Ir, Ni, Os, Pd, Tl, Zn, and some Te and Sb. The precipitate is decomposed by HNO_3. Osmium is distilled as OsO_4 (Leddicotte, 1961; Walsh and Hausman, 1963) into NaOH, and is further purified by a second distillation from H_2SO_4 - H_2O_2 solution (Chung and Beamish, 1968a,b). The residue from the first distillation is converted to chlorides (Ag precipitates and is removed for purification, Glendenin, 1951) and loaded onto an anion exchange column (≡A) in 3 *M* HCl containing Ce^{4+}. The initial effluent contains Ni, Co, Cu, Sc, REE; Ni is precipitated with dimethylglyoxime and purified by cation exchange (Fritz and Rettig, 1962). If desired, the REE can be recovered from this fraction after removal of the highly active Sc^{46} by cation exchange (Ebihara, 1985). The elements remaining on the column (In, Te, Zn, Cd, Tl, Ir, Bi, Pd, and Au) are then eluted sequentially (Kraus and Nelson, 1956; Strelow and Bothma, 1967; Crocket *et al.*, 1968). Most elements are purified by one or more additional ion exchange steps, followed by precipitation steps (Laul *et al.*, 1970a, b). Gold is precipitated with hydroquinone (Beamish *et al.*, 1937), and Pd, with KI (Beamish and Dale, 1938) followed by dimethylglyoxime.

The supernate contains Br, Cs, Ge, Rb, Re, Sb, Se, Sn, W, and the remaining Te. After acidification with HCl, Ge and Br are distilled off, and are separated by solvent extraction (Marinsky, 1961; Rayner, 1963). The distillation residue is treated with SO_2 to precipitate Se and Te (Wilson and Wilson, 1962), which are further purified by anion exchange. The solution is then loaded onto a second anion exchange column (≡B). The first effluent contains some or most of the W [which is coprecipitated with $Fe(OH)_3$ and is then further purified] and Rb, Cs [precipitated as tetraphenyl borates (Geilmann and Gebauhr, 1953; Tomura *et al.*, 1968)]. The remaining elements Sb, Sn, and Re are eluted sequentially; the latter is purified by ion-exchange and precipitation (Anders *et al.*, 1959; Morgan, 1965).

MATERIALS AND TECHNIQUES

SAMPLES

Use powdered and finely divided material (e.g., U.S.G.S. standard rock powders or <1 mm lunar soils) as received, without further treatment. Other samples should be coarsely crushed to <2 mm size in an agate mortar. (Really fine grinding is not recommended, since this greatly increases the likelihood of contamination at the submicrogram level.) Prepare irradiation vials (~8 cm long) from high purity silica* tubing, 3 mm internal diameter with 1 mm wall. Clean in hot nitric acid, then aqua regia and wash at least 6 times

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*Suprasil quartz tubing, suppling by Amersil, Inc., Hillside, New Jersey.

with distilled water. Drain out as much water as possible; use some acetone. Dry in an oven, cool and weigh. Load the sample into a weighed tube, reweigh and seal to a length of 5 cm.

STANDARDS

Prepare stock solutions for the required elements. Appropriate gravimetric forms are given in Table 2. In order to maximize use of space in the irradiation capsule it is convenient to prepare mixed monitors. Typical combinations are Ag-Se-Pd, Ni-In-Zn-Cd-Au, Te-Tl-Bi, Br-Cs-Rb, Ge-Sb-Sn-Re, Ir, Os-W. For U, the U.S.G.S. standard basalt BCR-1 is used.

Prepare dilute working standard solutions, containing the combination of elements in concentrations as given in Table 2. Determine the density of the working standard and calculate the weight concentration (μg/g).

Weigh 0.05 to 0.10 g of solution into clean silica vials (see Samples). Add 20-50 mg of specpure MgO to each vial. (This inert diluent reduces recoil and self-shadowing problems during irradiation.) Evaporate the solutions to dryness in an oven, initially at 60°C and gradually increasing to temperatures of 80-90°C when nearly dry. Seal the vial at a length of 5 cm. Calculate the weights of the standards and record.

CARRIERS

Prepare carriers for all elements to be determined (except U, which is determined via fission Te). The weighing forms used for monitor preparation are suitable, but analytical grade rather than specpure chemicals should be used. The carrier solution should be just sufficiently acidic to prevent hydrolysis (except for Br, Ge, and Sb, which should be in neutral solution if the weighing forms from Table 2 are used). Typical concentrations, weighing

TABLE 2. Preparation of standard solutions

Element*	Weighing Form	Treatment	Stock Solution		Dilute Working Standard		Amount Irradiated
			Acid Conc	Element mg/ml	Stock Solution ml	Final Volume ml	µg
Ag	Ag metal[a]	conc. HNO_3	8 *M* HNO_3	2	3	250, 0.4 *M* HNO_3	4
Se	H_2SeO_3[b]	-	0.5 *M* HNO_3	2	2		3
Pd	Pd metal[b]	aqua regia	1 *M* HCl	7	10		20
Ni	Ni metal[e]	HNO_3	1 *M* HCl	40	4	100, 1 *M* HCl	300
In	In metal[d]	8 *M* HNO_3	1.5 *M* HNO_3	1	5		5
Zn	Zn metal[e]	dil HCl	0.1 *M* HCl	3	2		10
Cd	Cd metal[a]	8 *M* HNO_3	0.1 *M* HCl	3	5		20
Au	Au metal[b]	aqua regia	1 *M* HCl	1	2		3
Te	Te metal[b]	8 *M* HNO_3	1.5 *M* HNO_3	4	2	100, 2 *M* HNO_3	8
Tl	$TlNO_3$[b]	-	0.2 *M* HNO_3	2	2		4
Bi	$Bi(NO_3)_3 \cdot 5H_2O$[c]	-	2 *M* HNO_3	2	10		20
Ge	$(NH_4)_2Ge(C_2O_4)_3 \cdot 4H_2O$[b]	-	H_2O	2	2	250, H_2O	2
Sb	$K(SbO)C_4H_4O_6 \cdot \frac{1}{2} H_2O$	-	H_2O	2	5		5
Sn	$(NH_4)_2SnCl_6$	-	H_2O	2	10		20
Re	NH_4ReO_4[b]	-	H_2O	2	2		2
Br	$NaBrO_3$	-	H_2O	4	10	50, H_2O	80
Rb	RbCl[b]	-	H_2O	4	10		80
Cs	CsCl[b]	-	H_2O	1	2		4.5
Os	$(NH_4)_2OsCl_6$[b]	3 *M* HCl/SO_2	3 *M* HCl/SO_2	1	5	100, 3 *M* HCl	5
W	$Na_2WO_4 \cdot 2H_2O$	-	H_2O		2		2
Ir	$(NH_4)_2IrCl_6$[b]	-	0.2 *M* HCl	1	2	250, 3 *M* HCl	5

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*For U, BCR-1, is used as monitor.
a) Matheson, Coleman and Bell; b) Johnson-Matthey specpure, spectrographically pure; c) Fisher certified; d) Tadanac, high purity; and e) Baker analyzed.

forms, and treatment of carrier solutions are given in Table 3. Check the Cs^{137}-tracer for Cs^{134}-activity and correct for its contribution if necessary.

Take an appropriate number of clean Zr crucibles (number of samples +1 for each set - it saves time to prepare 2 sets at the same time) and moisten the inside with 10 drops 6 *M* NaOH. Evaporate to dryness under a heat lamp.

Pipet suitable aliquots of carrier solution, in order of increasing acidity (see Table 3). After the addition of each carrier, add a slight excess of 6 *M* NaOH, and evaporate to dryness under a heat lamp. The preparation of the crucibles takes about one week when 21 elements need to be pipeted. Store the crucibles under vacuum in a desiccator until required; the longer they can be stored under vacuum, the better (see treatment of the samples). Preferably, start crucible preparation about 2 weeks before starting the chemistry.

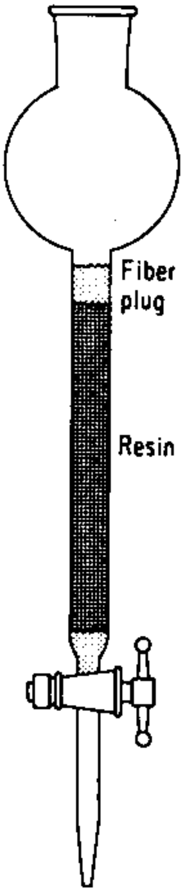
It is imperative to make the solution basic with NaOH after each addition of carrier, otherwise the HNO_3 *in the carrier attacks the Zr metal, causing holes to appear during fusion! Add enough excess NaOH to keep the solution basic at all times; since the pH cannot be checked without causing loss of carrier, calculate the amount of NaOH needed, and add an excess, to be on the safe side.*

Table 3. Carriers

Element	Weighing form	Treatment	Final Solution	Typical amount mg
Re	$KReO_4$	-	H_2O	15
Sb	$K(SbO)C_4H_4O_6\cdot \frac{1}{2} H_2O$	-	H_2O	40
Zn	$ZnCl_2$	-	0.1 M HCl	30
Cd	$CdCl_2\cdot 2 \frac{1}{2} H_2O$	-		30
Au	Au-metal	aqua regia/HNO_3		40
Se	Na_2SeO_4	-	1 M HNO_3	40
Ir	$(NH_4)_2IrCl_6$	1 M HCl	0.2 M HCl	10
Ni	Ni-metal	7 M HNO_3	0.4 M HNO_3	20
Bi	$Bi(NO_3)_3\cdot 5H_2O$	3 M HNO_3	0.5 M HNO_3	40
In	In-metal	conc. HNO_3		40
Tl	$TlNO_3$	-		40
Ag	$AgNO_3$	1 M HNO_3	1 M HNO_3	50
Pd	$PdCl_2$	aqua regia	0.1 M HNO_3 1 M HCl	20
Te	$Na_2TeO_4\cdot 2H_2O$	-	2 M HCl	40
Rb	$RbNO_3$	-	2 M HCl	20
Cs-Cs^{137}	CsCl	-		20
Br	KBr	add few mg $KHCO_3$	H_2O	40
Os	$(NH_4)_2OsCl_6$	-	3 M HCl	6
Ge	$(NH_4)_2Ge(C_2O_4)_3\cdot 4H_2O$	-	3 M HCl	40
Sn	$SnCl_2\cdot 2H_2O$	-	3 M HCl	30
W	$Na_2WO_4\cdot 2H_2O$	-	H_2O	40

NOTES ON ION EXCHANGE SEPARATIONS

Throughout this procedure, directions for ion exchange separations are given for nominal columns of a specific length, diameter, and flow rate. A typical column is shown in the accompanying figure. The procedures have generally been rehearsed for these or similar columns, and were scaled to the exact dimensions of the nominal columns. Elution volumes are given both in ml and "gross column volumes" (v = area x height of resin bed). Actual elution curves are included in the text, whenever available. Where known, 3 parameters are given, all in units of V:



V_{50} = Volume required to elute 50% of the species sought.

V_{99} = Volume required to elute 99% of the species sought.

V = Recommended volume for a cut.

When "est." is listed after a numerical value, then this value is based on published volume distribution coefficients (D_v), rather than an actual tracer experiment by the authors. The V values in such cases are very conservatively chosen, and should be ample enough to preclude any loss. If v for the actual columns differs from the nominal v by more than ±5%, then V should be recalculated accordingly. In general, volumes specified for nominal columns can be scaled to columns of different dimensions, using v as the scaling factor. Care must be taken, however, not to overload the column (we prefer to load to <20% of capacity) or to use appreciably faster flow rates (≤2.5 cm/min for preliminary separations and 0.5-1 cm/min for purification or large load volumes seem good choices). The general columns A and B have especially small safety margins, having been designed close to minimum size in the interest of speed. It is therefore essential to keep volume and concentration of the load solution close to specifications or else ions with small D_v (Sb, Re, Pd) will "break through" and elute prematurely or spread over several fractions.

The proportions of the column depend on the nature of the separation. Short columns (length/diameter <20) may be used for separations involving simple "selective displacement", [where one element has a small D_v (≤2) and therefore emerges in a few column volumes, whereas the other elements, having large D_v (>10), remain stuck at the top of the column]. For more delicate chromatographic separations, where the element is eluted more slowly ($D_v \approx 10$), and both the preceding and following fractions are discarded, long columns, slow flow rates, and fine resin should be used, and the elution volumes should be scaled to the actual v.

It is advantageous to use 200-400 mesh resin for most separations. This gives sharper separations than coarser resin, because the number of theoretical plates is inversely proportional to the resin bead diameter. Flow rates still are adequate (>0.8 cm/min) at column lengths up to 12 cm. Even for the general columns A and B, where speed is essential, such flow rates are acceptable and actually deliver fractions at a more manageable pace than a faster column of coarser resin.

Two pointers on technique: 1) Before inserting the dacron or glass wool plug at the top of the column, make sure no resin particles are stuck to the walls, otherwise they will get caught in the plug. 2) After loading a solution on the column and washing it with the specified few ml of wash solution, rinse the column reservoir at least twice with water or dilute acid, to remove any adhering traces of activity that would otherwise contaminate the effluent. Pour the wash liquid into the reservoir (fill it to the top if you like) swish it around to rinse the walls and then discard. Repeat, then remove the last traces of wash liquid with a Pasteur pipet, so that the wash liquid does not penetrate into the plug or resin.

PROCEDURES*

A. FUSION AND SULFIDE PRECIPITATION

When the irradiated samples are ready for opening, clean the outside of each vial (except for standards) in aqua regia and wash with distilled water. Add 2 g of Na_2O_2 and 1 g NaOH pellets to each Zr crucible. Open the vial and transfer the sample to the crucible. Add a further 2 g of Na_2O_2 and cover the crucible with a Zr lid, allowing a gap of ~3 mm at one side. Heat over a Meker burner at very low heat for about 5 minutes until all H_2O is driven off. (If the crucibles have been stored for several days in a vacuum, this step proceeds very smoothly.) Close the crucible completely. Gradually heat to a dull red color and continue fusion for about 20 minutes. Swirl the melt every few minutes to assist in dissolution and mixing. Allow to cool for 10 minutes.

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*The actual working procedure is given in roman type. *Explanations, comments, and background information are given in italic type.*

Remove the lid from the crucible and wash with a fine jet of water, allowing the washings to run into a 250 ml beaker. Try to use no more than 10 ml. Wash the outside of the crucible with water and discard washings. Stand the crucible in the beaker and cover the latter with a watch glass. Add ~50 ml distilled H_2O to the crucible and wait (possibly overnight) until the melt has dissolved. Remove the crucible from the beaker and wash with H_2O, allowing the washings to run into the beaker. Add ~2 ml of 1:1 H_2SO_4 to the crucible and heat to white fumes over a burner. Cool, dilute with 10 ml of water, and transfer the solution to the beaker. (This solution is usually blue due to Ir.) The total volume at this stage should be no more than 70-80 ml. Check the pH of the solution, which should be strongly alkaline (pH>10).

Add a drop of ~1 *M* $MnCl_2$ solution (to produce MnO_2 that will catalyze decomposition of peroxide). Insert a magnetic stirring bar, cover the beaker, place on a stirrer hot plate, and heat to near boiling until O_2 evolution has ceased (≤15 minutes). Dropwise, from a burette, add sufficient 1 *M* Na_2S (i.e., 24 g $Na_2S \cdot 9H_2O$/100 ml solution) over 1.5-2 minutes to precipitate the insoluble sulfides completely and to convert Re, Sb, Sn, Ge to their soluble sulfosalts. ***For the amounts of carrier listed in Table 3, the stoichiometric amount (including sulfosalts) is 14.4 meq, so 10 ml of 1 M*** Na_2S ***should be ample, provided that all peroxide was destroyed.*** Check that precipitation is complete, and add 5-15 drops of 3 *M* $MgSO_4$. Heat and stir for 15 minutes; the $Mg(OH)_2$ precipitate will carry down any colloid. Cool in a cold water or ice bath.

Faster precipitation (10 sec) leaves more Ge and Sb in the supernate (97 vs 89% and 89 vs 72%), but mainly in colloidal form. When the colloid is coagulated, there is little difference in yield. The amount of $MgSO_4$ should be kept as small as possible, because $Mg(OH)_2$ carries Ge. The amounts remaining in the supernate, after scavenge with 1.5 mM $MgSO_4$, are:

	Ge	*Sb*	*Sn*	*Te*
Before(%)	*89;83*	*72;78*	*93*	*70.4*
After (%)	*76;70*	*69;75*	*89*	*70.1*

A 15-minute leach of the precipitate with 10 ml 1 M NaOH recovered only 2% Ge and 1.5% Sb (of the total).

The behavior of Te depends on the temperature (Noyes and Bray, p. 326). At room temperature, it forms TeS_2, which slowly dissolves in excess NaOH-Na_2S, but on heating, it gradually decomposes to Te, which is insoluble. A tracer experiment gave 59% Te in the supernate after the usual 2 minutes precipitation and 15 minutes heating, but 70% after another 30 minutes at 100°C, with stirring.

Transfer the solution and precipitate to a 250 ml centrifuge tube. Rinse the beaker with the minimum amount of H_2O and spin down. *(The solution is evaporated to 40-50 ml later, so keep the volume small.)* Transfer the supernate to a 250 ml beaker and keep both fractions for further treatment. The solution should be light yellow. The mixed sulfide-hydroxide precipitate contains Ag, Au, Bi, Cd, In, Ir, Ni, Os, Pd, Tl and Zn together with ca. 40% of Te and 30% of Sb. The supernate contains Br, Cs, Ge, Rb, Re, Se, Sn, W, and remaining Sb and Te.

B. THE MIXED SULFIDE-HYDROXIDE PRECIPITATE

1. The Distillation of Os

Cool the sulfide-hydroxide precipitate in an ice-bath and dropwise add 20 ml concentrated HNO_3*, stirring the mixture.

Transfer the solution into a 100 ml round-bottomed, short-neck distillation flask, washing with 10 ml water. (The HNO_3 concentration for distillation should be about 6 *M*). The still, made from 6 mm I.D. glass tubing, is attached to the distillation flask with a ground-glass joint and supplied with an air inlet tube passing down to near the center of the flask. The outlet tube from the flask has a 20 cm horizontal section, terminating in a 35 cm vertical arm.

Using a heating mantle at a Variac setting of 80 V, distill at a rate of 1-2 ml min^{-1} in a gentle flow of air (1-2 bubbles/sec).

Collect OsO_4 in a boiling tube containing 20 ml of 6 *M* NaOH and cooled in an ice-bath. After about 10 min (when nitrous vapors no longer are evolved) the NaOH solution is colored pale yellow to orange. Continue the distillation for another 20 min. If decoloration occurs before the end of this period, stop the distillation immediately and add some more 6 *M* NaOH to the boiling tube in order to prevent loss of OsO_4. Seal the tube with parafilm and store in refrigerator until Os samples can be purified.

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*All acids used are concentrated, unless otherwise specified.

Transfer the residue in the distillation flask back into the 250 ml beaker, using a minimum quantity of distilled water, and place on a warm hot plate (plastic glove must not stick to it). Cover the beaker with a watchglass.

2. Conversion to Chlorides

(a) Add 2 mg Co carrier and 20 ml HCl to the beakers. Digest the precipitate for several hours or overnight, add 1-2 ml 5 *M* LiCl, and then allow to go to near dryness. Add 10 ml HCl and again evaporate to near dryness. Repeat this evaporation at least twice with 5 ml HCl, until every trace of nitrogen oxides has been removed.

Repeated evaporation is needed to convert nitrosyl complexes of Ir, which tend to elute prematurely, to well-behaved $IrCl_6^{3-}$. *The addition of LiCl aids this process, by providing a high* Cl^- *concentration in the last stages of evaporation.*

If the samples are overheated or contaminated with traces of organic matter, reddish specks of metallic Au will form. If this happens, dissolve the Au in a few drops of aqua regia, and evaporate at least twice with HCl to remove all traces of nitrate.

(b) Prepare an anion exchange column, 1 x 12 cm (v = 9.4 ml), using Bio-Rad AG1-X10 resin, 200-400 mesh, Cl^- form, and dacron plugs. Condition the column first with 15 ml 0.5 *M* HCl + 0.1 *M* Ce(IV) (freshly mixed from a stock solution of 0.2 *M* $Ce(SO_4)_2$ in 1 *M* H_2SO_4), until yellow Ce(IV) appears in the effluent, then with 30 ml 3.5 *M* HCl.

The exposure time of Ce(IV) to HCl and resin must be minimized, because Ce(IV) slowly oxidizes HCl to Cl_2, *especially at [HCl] > 1 M. The* Cl_2 *interferes in the procedure by oxidizing Te from +4 to +6, and by degrading the resin to species that complex with Ir and change its anion exchange behavior.*

3. Separation of Ag and Loading of Column A

Dissolve the residue from step 2 (a) in the minimum volume (~12 ml) of 3.5 *M* HCl, by warming on a hot plate for a few minutes. A white precipitate of AgCl (and some SiO_2 and $BaSO_4$) remains at this point. [Reddish specks indicate metallic Au, which must be redissolved according to the note in 2 (a)]. Cool and add 1 ml 0.2 *M* $Ce(SO_4)_2$ in 1 *M* H_2SO_4, to oxidize Ir from +3 to +4, and ~0.1 ml of 10 *M* HF, to complex Pa^{233}. These small amounts of fluoride attack the glass column only to a slight extent; plastic receivers should be used for the last 2 fractions, however.

Centrifuge and filter the supernate through Whatman 541 paper onto the anion exchange column. Wash the precipitate with 8 ml 3.5 *M* HCl + 1 drop 10 *M* HF, centrifuge, filter the supernate onto the column, and save the precipitate for Ag purification.

Start the Ir oxidation only if you have time to complete the loading, washing, and first elution step immediately afterwards, so that exposure of solution and resin to Ce(IV) is minimized. The loading and washing step should be done from the minimum amount of solution (no more than 1.5 v + 1 v), and at the slowest practicable flow rate, to keep the adsorption band sharp and narrow. The maximum flow rate of a 12 cm, 200-400 mesh column (~0.8 cm/min) is acceptable, but if time permits, use a flow rate of ≤0.5 cm/min.

4. Anion-Exchange Separation of
Au, Bi, Cd, In, Ir, Ni, Pd, Te, Tl, and Zn

Elute according to the following table, at a flow rate of ≤1 cm/min. The principal activities are REE, Co^{60}, and Fe^{59}, so use reasonable precautions until these species are eluted, and store the active fractions behind lead bricks.

4.1. Background Information on Column A

The elution volumes were determined for a 1x10 cm, 200-400 mesh column at a slow flow rate (0.9 cm/min) and a high degree of loading (20-24%), and are not strictly applicable to columns of other dimensions or operating *conditions. The safety margins for V are large enough so that we were able to use the same V's for a 12 cm column, but the* V_{50}*'s and* V_{99}*'s for such a column (of smaller loading) must be somewhat larger than those for a 10 cm column given in the table. The first 4 steps (through In) have been rehearsed with tracer for a 12 cm column and [HCl] = 3.5 M, so the values given for these very critical fractions are accurate.* V_{50} *for In includes the wash soln. and the pre-In fraction.*

The adsorption bands follow the order of D_v*'s in 3 M HCl:*

Au	*7×10^5*	*yellow*	*Zn*	*1700*	
Tl(III)	*1×10^5*		*Te(IV)*	*1000*	
Ir(IV)	*~3000*	*dark brown*	*Fe(III)*	*1000*	*orange brown*
Cd	*3000*		*Pd(II)*	*430*	*reddish brown*
Bi	*2200*		*In*	*22*	

When loaded at a flow rate of 0.9 cm/min, the Pd band appears at 3.7 cm, though the 1.95 meq carriers (exclusive of In) theoretically require only 1.3 ml = 1.6 cm of resin. Thus only 6.3 cm of resin is available for adsorption of weakly-held In, and for development of all species. Things are a little worse in an actual run because some 0.5 meq Fe^{3+} *must also be accommodated, and for this reason we prefer use 12 cm columns. It is essential to keep volume and flow rate to a minimum during the loading step, and not to skimp on column length.*

This is especially important for In and Pd. Under proper conditions, the In adsorption band extends from the Pd band to somewhat above the base of the column, permitting the elution of 2 column volumes of a pre-In fraction containing REE, Co, Pa, and other highly active species. If load volume and flow rate are larger, or if the column is shorter, then the In band will extend to the base of the column, causing In to appear in the pre-In fraction. The present procedure does have a small safety margin, because In normally begins to elute only after 3-4 v of 3.5 M HCl (including the 2 v of the pre-In fraction), but this margin will shrink rapidly if load volume and flow rate exceed specifications.

The Pd band moves appreciably during elution of Ir and Bi, and normally is within 4 cm of the base of the column by the time Pd elution starts. It will elute prematurely if column parameters are changed in the wrong direction.

5. Precipitation of Te

To the 28 ml Te, Fe fraction from column A, add 4.5 ml HCl to raise acidity to 2 *M* and bubble SO_2 through solution for 10 minutes, to reduce Te to the metal. Centrifuge, and retain the precipitate for processing with the Te fraction from the Ge distillation. *(The anion exchange procedure used for Te purification does not separate Fe from Te, because both have very similar*

D_v's. Thus Fe will have to be removed by washing, after the precipitates have been combined.)

6. Precipitation of Ni

(a) Transfer the combined effluent and washes (48 ml) from ion exchange column A into a 250 ml centrifuge tube. (Recall that the solution contains HF, so minimize exposure to glass.)

(b) Add 10 mg Fe, 2 mg Co, and 2 mg Mn carriers, stir and neutralize with 6 *M* NH_3 until $Fe(OH)_3$ begins to precipitate at pH 3 (about 28 ml may be required), then add 4 ml in excess. The final pH in this buffered solution should be between 8 and 9 ($[NH_3] = 0.2\text{-}0.3$ *M*; $pH = 9.25 - \log[NH_4^+]/[NH_3]$).

(c) Centrifuge, transfer the supernate into a clean centrifuge tube, and discard the highly active precipitate, or save it if REE are to be analyzed. [*The main activities, Fe^{59} and Sc^{46}, can be conveniently removed by a cation exchange step; (Ebihara, 1985)*].

(d) To the supernate, add 2 ml of 1 *M* citric or tartaric acid solution (to complex any remaining trivalent cations), and stir.

(e) Add 25 ml dimethyglyoxime (DMG) (1% in 95% ethanol) and a few drops of a wetting agent to the supernate. Retain the red $Ni(DMG)_2$ precipitate and discard the supernate, after testing for completeness of precipitation. Thoroughly wash the precipitate with 2-3 50 ml portions of H_2O, to remove the bulk of the Co activity. Centrifuge, discard the supernate, and process according to In-Ni purification procedure (see In purification).

C. SEPARATION OF Cs, Ge, Rb, Re, Sb, Se, Sn, AND Te

The supernate from the initial hydroxide-sulfide precipitation contains Br, Cs, Rb, Re, Se, Sn, about 70% of Ge and Sb and about 50% of Te. (Other elements expected in this fraction that form n,γ or n,f nuclides of more than 12 h half-life include Be, Na, P, S, Cl, K, Ca, Ga, As, Mo, W, and I.) The

ELUTION SCHEDULE FOR COLUMN A
(AG-1-X10, 200-400 mesh, 1 x 12 cm, v = 9.4 ml, flow rate 0.8 cm/min)

Volume ml	v	V_{50}	V_{99}	Reagent	Species Eluted	Disposition	Notes	Fig.#
≤12	≤1.3			Load (3.5 *M* HCl + Ce^{4+} + HF)	Ni,Co,REE Mg,Pa,Cr, Mn,F^-	Ni pptn.	ab	
≤ 8	≤0.9			Wash (3.5 *M* HCl + HF)				
28	3			3.5 *M* HCl - 0.05 *M* HF				
94	10	4.4	9	3.5 *M* HCl	In, F^-	In-Ni pur.	b	1
28	3		2	0.5 *M* HCl	Te, Fe	Te pptn.	c	
75	8			0.5 *M* HCl	Fe	Discard	d	
42	4.5	1.5	3.3	0.03 *M* HCl	Zn	Zn pur.	ae	2
132	14	7.7	11.3	0.001 *M* HCl	Cd	Cd pur.	af	3
115	12	5.8	10.3	0.1 *M* H_2SO_3*	Tl	Tl pur.	g	4
115	12	<3	9.8	6 *M* HCl	Ir	Ir pur.	h	5
20	2			H_2O	HCl	Discard	a	
94	10	6	9	1 *M* H_2SO_4 - 0.003 *M* HCl	Bi, Cl^-	Bi pur.	i	6
19	2			*Aqua regia* - H_2O (1:1)	-	Discard	j	
28	3			H_2O	(Ir)	Discard		
57	6	2.7	?	1 *M* $HClO_4$ - 0.003 *M* HCl	Pd	Pd pur.	ak	
10	1			H_2O	$HClO_4$	Discard		
94	10			10% thiourea	Au	Au pur.	al	

**Use 60 ml saturated SO_2 soln. per 1000 ml.*

Notes on Elution Schedule for Column A

(a) Thoroughly rinse reservoir before adding eluent. Use plastic receivers for fractions containing F^-.

(b) About 7% of the Ir appears in these two fractions; much more if NO-complexes were not destroyed, or were allowed to re-form. Some Zn (2%) and Cd (1%) also elute, mainly in pre-In fraction.

(c) Ir contamination 0.1-1%.

(d) It is safe to use more than 8 v 0.5 M HCl to elute Fe, because Cd and Zn have high D_v's in 0.5 M HCl (2000 and 200). However, Fe(III), despite its D_v of 0.8, may be slow in coming off the column, so check whether a larger volume actually is better. Much of any Fe remaining should come off with Tl, after having being reduced to Fe(II).

(e) 4 v suffices for 99% recovery of Zn, but 6 v leaves less Zn in the Cd fraction. Ir contamination 0.06%.

(f) A white BiOCl band appears on the column at this stage. Ir contamination 0.04%.

(g) The H_2SO_3 reduces Au and Pd to the metals (gray to black), and $IrCl_6{}^{2-}$ (brown) to $IrCl_6{}^{3-}$ (yellowish green). Ir contamination 0.7%.

(h) About 80-90% of the Ir appears in this fraction.

(i) The 0.003 M HCl keeps the $PdCl_4{}^{2-}$ from dissociating; it is not needed if all the Pd was reduced to the metal by H_2SO_3. Larger amounts of Cl^- will significantly retard Bi, so be sure to rinse all traces of 6 M HCl from the reservoir. Ir contam. 0.3%.

(j) Use half-strength aqua regia; it is just as effective as full-strength in dissolving Au and Pd, but does not generate bubbles that clog the column. Some 2% of the Ir appears in the aqua regia fraction and associated H_2O wash.

(k) In rehearsals, when 0.1 M HCl-0.05 M Cl_2 was used instead of aqua regia to dissolve Pd, only 86-88% of the Pd was recovered, and the shape of the elution curve suggests that this was not due to normal tailing. Aqua regia gives better yields. Ir contamination 0.6%.

(l) Au elutes faster in neutral 10% thiourea (<10v) than in the traditional 0.1 M HCl-0.1 M thiourea medium (20-25 v).

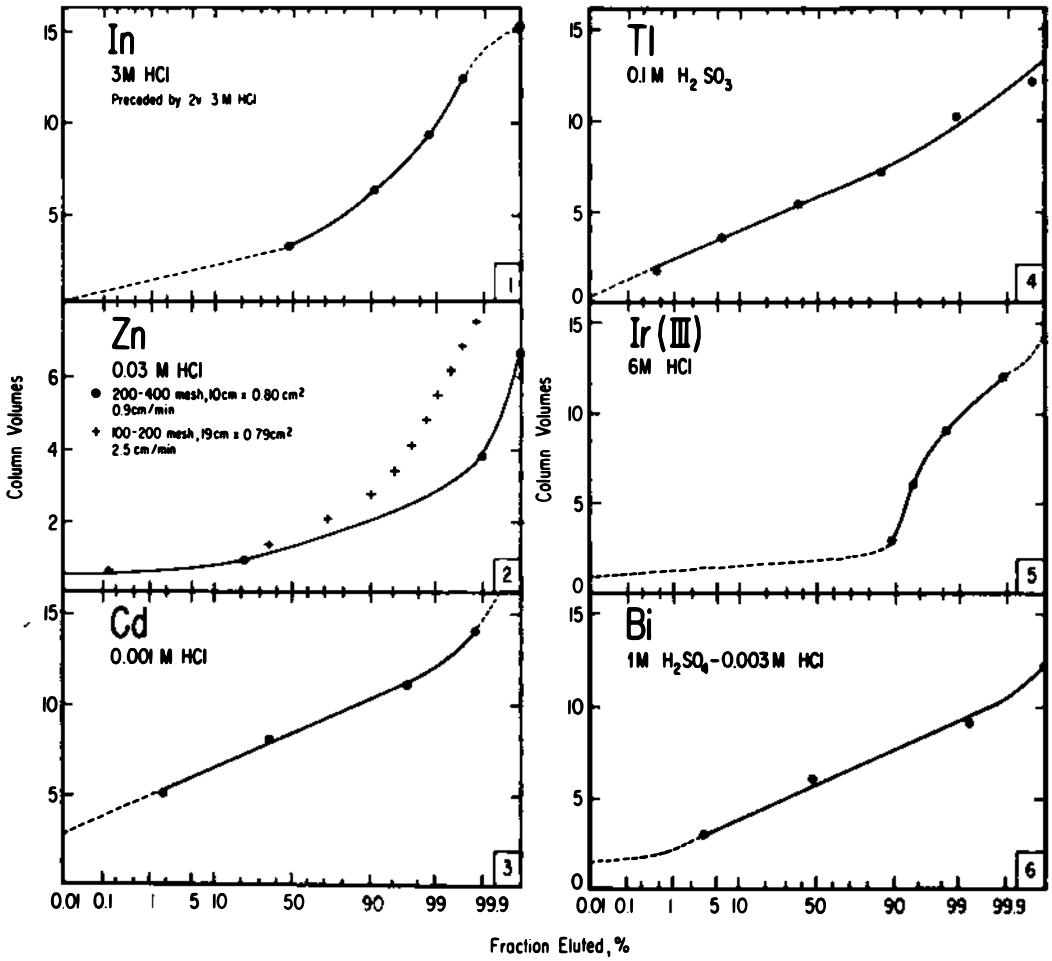
solution should be clear and light yellow, free of any traces of the sulfide-hydroxide precipitate. (This precipitate is far more active than the supernate, and contains some tenacious contaminants, such as Fe^{59} and Ir^{192}. It is therefore imperative to remove all traces of the precipitate, by careful decantation and other appropriate means. Possibilities include: (a) filtration; (b) two Mg(OH)$_2$ scavenges instead of one in Part B, but each with one-half the amount, to minimize loss of Ge).

1. Distillation of Ge

Assemble the stills beforehand, so that the distillation can be started immediately once the samples are ready. The still consists of a 250 ml round-bottom flask without air inlet and with a 24/40 joint, a still head and water-cooled condenser, and an ice-cooled 125 ml Erlenmeyer flask.

(a) Add 3 or 4 SiC boiling chips to the solution in a 250 ml beaker and evaporate to about 40-50 ml, when salts begin to crystallize. There is no harm in letting the evaporation go to dryness, but the solution may bump and the residue may be hard to dissolve. Cool and neutralize with 6 *M* HCl. (About 20 ml should be required; near the neutral point, the initially bluish green sulfide precipitate changes to yellow.) Add a sufficient excess of HCl to make [H$^+$] = 1 *M* HCl. Ignore the precipitate, and boil for a few minutes to expel H_2S and to dissolve the bulk of the sulfides. Add an extra 1/2 ml HCl to initiate the reaction if necessary. Stop when brown NO_2 fumes are no longer evolved. (The oxidation is effected by NO_3^- from the carriers, which generally survives the fusion.) Brief boiling should cause no significant loss of $GeCl_4$, as long as the acidity is not much above 1 *M*. Cool.

(b) When you are ready to start the distillation, accurately measure the volume of the first two solutions. Transfer them to 250 ml distilling flasks containing 6-8 boiling chips. Add sufficient HCl to the flasks to make [H$^+$] = 4-4.5 *M* (total volume should be around 100-200 ml), and immediately attach the still head.



Figures 1-6. Elution curves for Column A (Bio Rad AG1-X10, 200-400 mesh, 10 cm x 0.82 cm², flow rate = 0.9 cm/min). Data are plotted on probability paper, on which a Gaussian curve gives a straight line. Deviations from Gaussian shape are largest for In, which is weakly held, and for Ir, which undergoes complex chemical changes during reduction and elution.

The two curves for Zn show the superior performance of a shorter column with finer resin and slower flow rate, even though the elution times of the two columns are similar.

(c) Distill at 60 V until the solution is clear and pale-green, and no longer evolves NO_2. Raise the voltage to 80 V, and continue until 40 ml has distilled or the solution starts bumping -- whichever comes first. Tightly stopper the receiver with a ground glass stopper (Br_2 and NO_2 attack rubber) and store in refrigerator until you are ready to start the Ge extraction. *(Once As^{76} and Br^{82} have decayed, the activity of the distillate is quite low - typically $<10^4$ dpm).* Now acidify the next 2 samples, and process according to (b) and (c).

<u>Note 1.c.</u> According to Prestwood, only water but no $GeCl_4$ distills until [HCl] has risen to constant-boiling (= 6 M), but then $GeCl_4$ comes over rapidly. At higher HCl concentrations, $GeCl_4$ is swept out with HCl gas, and may not recondense. Bubbling of air, especially at rates of more than 2 bubbles/sec, is definitely harmful; Nelson and Kraus (1960) have found that $GeCl_4$ is swept out with a half-time of 2 minutes (!) when N_2 is bubbled at "a moderate rate" through 12 M HCl.

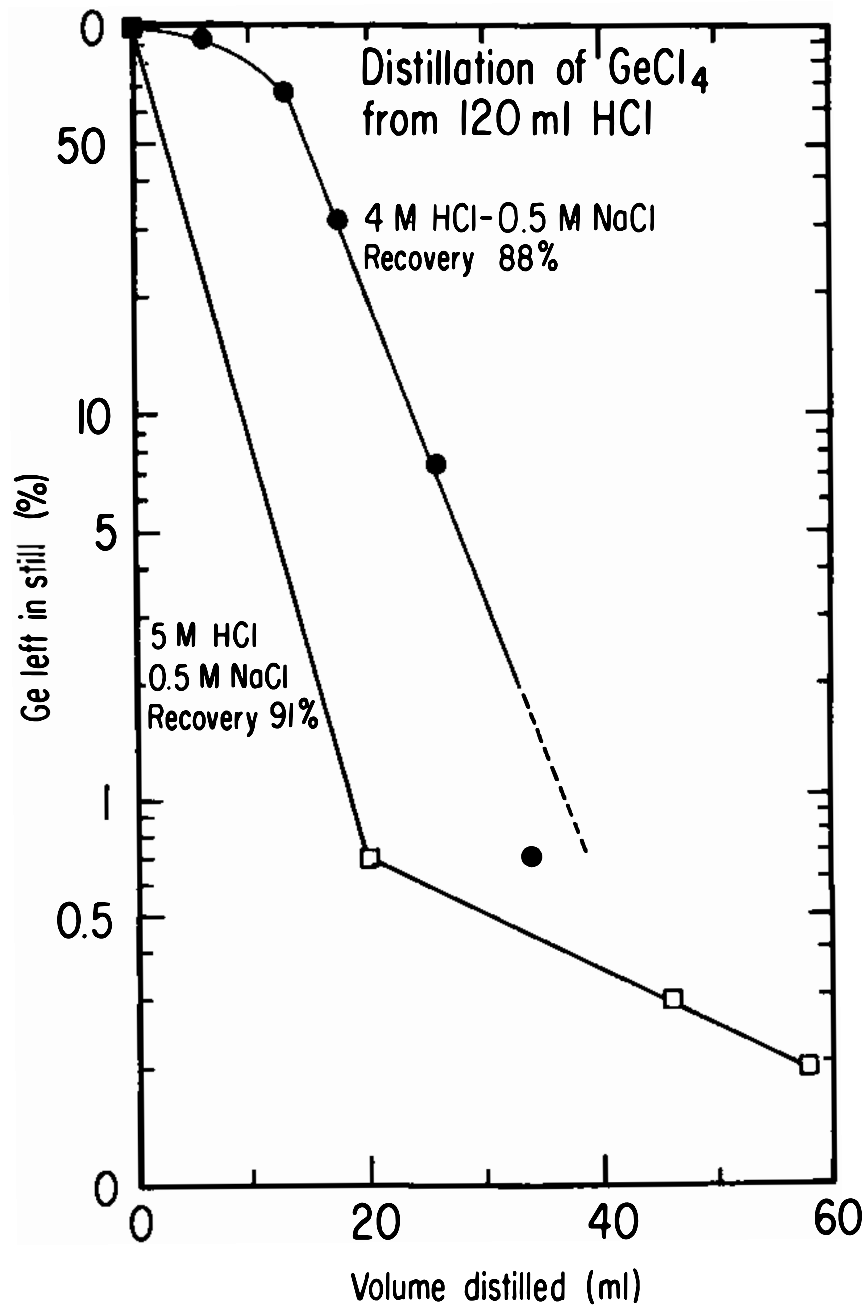
Because the solution contains excess Cl^-, distillation of $GeCl_4$ starts at $[H^+] < 6$ M. In one experiment with 120 ml 5 M HCl and the usual amounts of NaCl, 99.3% of the Ge distilled appeared in the first 20 ml. When the initial acidity was 4 M, only about 79% distilled in the first 20 ml, but the remainder distilled rapidly, with only 0.7% remaining after 34 ml (Fig. 7). The total recoveries in these experiments were only 91% and 88%, perhaps due to losses in the initial acidification, or incomplete condensation.

If Br is included in the procedure, then ~0.05-0.1 g $NaClO_3$ must be added to the flask before distillation, to oxidize Br^- to Br_2.

2. Separation of Ge and Br

Several hours before starting the experiment, refrigerate 1.5 liters of concentrated HCl, 0.6 liters of 9 M HCl, and 1 liter of CCl_4. Add 0.1-0.5 g $NaClO_3$ to each Ge distillate, to oxidize As(III) to As(V).

It is not necessary to pre-equilibrate the CCl_4 with HCl because the solubility of HCl in CCl_4 is only 0.027M from 12 M HCl, and less from more dilute solutions.



<u>Figure 7</u>. $GeCl_4$ distills more rapidly from 5 *M* HCl than from 4 *M* HCl. according to (b) and (c).

(a) Pour 35 ml chilled CCl_4 into a 250 ml Teflon-stoppered separatory funnel, shake a few times, release the pressure, and repeat until pressure buildup ceases. Add the ice-cold Ge,Br-distillate and twice its volume of chilled concentrated HCl. ($GeCl_4$ is very volatile from strong HCl solutions, so use ice-cold reagents and add the HCl last.) Immediately stopper the funnel and shake for three 15-second periods, separated by 1-minute intervals. Do not vent the funnel, but relieve pressure by draining the first few ml of the CCl_4 layer into (b) with the stopper closed.

(b) Let stand until the phases have separated, then drain the organic layer into a 125 ml funnel containing 30 ml chilled 9 *M* HCl. Repeat the extraction with a fresh 35 ml portion of CCl_4, but with less extreme precautions: shake for 30 seconds, let phases separate, and add the organic phase to the first extract in the 125 ml funnel. (D_{Ge} and D_{Br} are about 300 and 23, so 2 extractions should recover 99.9% of the Ge and 98% of the Br.) Discard the aqueous phase. Wash the combined organic extract with the 30 ml 9 *M* HCl in the 125 ml funnel, repeat once (in another 125 ml funnel) and discard the washings. Use extreme care during washing -- remember that $GeCl_4$ is as volatile as CCl_4.

Notes 2.a,b. The steps for Br have not been checked or optimized, because this element was no longer being measured when this procedure was last revised. If Br is to be measured, care must be taken to maintain oxidizing conditions during the distillation (e.g., use sufficient $NaClO_3$) and in the distillate and washings (make sure free Cl_2 is present, but that Br_2 is not oxidized to BrO_3^-). Moreover, Br_2 extracts poorly from 9 M HCl -- hence dilute the aqueous layer after Ge extraction and re-extract.

Extraction of Ge requires [HCl] ≥8M: D_{Ge} is 0.24 in 6.3 M HCl but 125 in 8.3 M and 597 in 10.3 M (Marinsky, 1961). However, a tracer experiment by R. Wolf gave D ~40 after 1 minute's shaking. The total yield was only 79%, probably due to insufficient cooling during acidification.

Arsenic (III) also extracts under these conditions (D ~2.7 in 9.5 M HCl). The (n,γ) product As^{76} normally is of no concern because of its 27 hour half-life, but the fast-neutron product As^{74} [17.8 d; made by As^{75} (n,2n) or Se^{74} (n,p)] could be troublesome. Because As(V) neither distills nor extracts, interference by As can be avoided by maintaining an excess of $NaClO_3$

during the distillation. However, this may be difficult in view of the large amounts of sulfur, and so a second line of defense is to add $NaClO_3$ to the distillate, thereby oxidizing As(III) to As(V).

(c) Back-extract Ge into 20 ml H_2O. Save the Br_2-containing organic layer if Br is to be measured. Transfer the aqueous layer to a centrifuge tube, add 1-2 ml of 3 *M* $NH_2OH \cdot HCl$, to reduce traces of Cl_2 and Br_2, and acidify to 3-4 *M* HCl with 8 ml concentrated HCl. Add 4 ml 13% thioacetamide (TAA), stir (but see Note 2.c) and seal the tube with parafilm. Allow to stand for at least 24 hours. (GeS_2 tends to be colloidal and very difficult to filter unless it is given several hours to coagulate.) Filter, wash, and mount according to step 1 of the Ge purification procedure. The samples should be radiochemically clean at this stage, and require no further purification.

Note 2.c. Fresenius and Jander (Ge volume, p. 8) recommend adding the thioacetamide solution (4%, 3.5 ml for each 10 mg Ge) cautiously to the top of the tube, so it forms a distinct layer on top. This yields a rather coarse, easily filterable precipitate.

(d) Combine the several Br_2 extracts and back-extract Br into 20 ml 0.05 *M* $NaHSO_3$ (freshly prepared from a reliable, 1-2 *M* stock solution). Add more HSO_3^-, a few drops at a time, if the Br_2 color persists in the organic layer; this may happen when much Cl_2 is present. Discard the organic layer, and save the aqueous layer for Br purification.

3. Precipitation of Se and Te

(a) Decant the solution in the distilling flask (~80 ml, ~6 *M* HCl) from the residue (NaCl, S, SiO_2). Wash the residue with 15 ml H_2O, add H_2O to make [HCl] ≈4 *M*, combine the washing with the solution, and save the residue. Filter the solution into a 250 ml beaker. The volume should be <120 ml, else the adsorption band on Column B will be too broad, causing premature elution of Re, W, and Sb.

A tracer experiment shows that after decantation, the ppt. retains a uniform 7-8% of all elements from the solution, mainly as interstitial liquid. A single wash removes most of it, except for ~ ½ of the W. The NaCl residue can be dissolved in H_2O and combined with the Cs-Rb fraction from Column B, but this may not be necessary, as only a small, constant fraction of Rb and Cs (~8%) is contained in the NaCl residue, and most of it apparently in interstitial liquid that should be removable by a single wash.

(b) Bubble SO_2 through the solution for about 10 minutes (about 4 liters SO_2 is required to saturate 100 ml of H_2O). Add 1 ml of 15% hydrazine hydrochloride ($N_2H_4 \cdot HCl$) solution, and cautiously heat to boiling for 5 minutes, to coagulate the Se, Te precipitate and expel some of the SO_2. Add Aerosol wetting agent, centrifuge, and save the solution for step (c). Save the precipitate for the Te-Se separation (see Te purification).

The HCl concentration is a compromise between the optimum for Te (2.6-2.9 M) and Se ($\geq$3.4 M). Hydrazine hydrochloride makes the precipitation of Te more quantitative. The boiling step, adopted from Wilson and Wilson, is supposed to serve the same purpose. It is essential, else some samples may post-precipitate Se on the column.

The SO_2 treatment also reduces Sb(V) to Sb(III), which is essential for the ion exchange separation.

(c) To the solution from (b), add ~ ¼ teaspoon Celite filter aid (diatomaceous earth), stir, and filter into the column reservoir. *The filtration removes silica, which otherwise clogs the column.* Load this solution onto anion exchange column B.

4. Anion-Exchange Separation of Rb, Cs, Sb, Sn, Re

Ga, As, Mo, and W are also present in the load solution and can be included in the procedure if desired. However, the steps for the first 3 elements have not been checked, and the behavior of W has not been brought under full control.

Prepare a plastic ion exchange column, AG1-X10, 200-400 mesh, Cl-form, 14.9 x 0.79 cm (v = 7.3 ml), with dacron fiber plugs and 250 ml reservoir. Condition the column with 30 ml 4 *M* HCl, and elute according to the following table.

The column itself consists of a plastic 10 ml serological pipet (Falcon brand). The reservoir is a 250 ml plastic bottle with the bottom cut off, which is attached to the column by a 1-hole rubber stopper. The dacron plug is made of pillow stuffing. Ideally, the column should be shorter but thicker (~10 x 1.2 cm) for a larger capacity and faster flow rate, but the plastic pipets used for the columns are available only with an ID of 0.79 cm.

It is essential that the volume of the load solution be as small as possible (<120 ml), so Sb and Re do not elute prematurely. If the volume is larger, reduce it by boiling (this is advisable anyway, as it expels SO_2 *and precipitates any remaining Se that would otherwise precipitate on the column).*

D. PURIFICATION OF INDIVIDUAL ELEMENTS

Chemical yields quoted in this section are for the first Chicago run using a preliminary version of this procedure. Later runs, with the final version of the procedure, generally gave better yields.

Antimony

1) Check Ga-Mo fraction (36 ml) from Column B for Sb activity, and combine with Sb fraction, if necessary. Next check γ-spectrum of Sb fraction from Column B (44 ml 0.3 *M* HCl-1 *M* HF). If clean, proceed to step 5, otherwise to step 2. [If a Ge(Li) detector is available for Sb counting, then proceed to step 5, whether or not samples are clean.]

2) Transfer solution to a 100 ml plastic beaker and add 2 mg each of Zn^{2+}, Co^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, and Ir(IV) holdback carriers. Make basic to ~0.5 *M* OH^- with 6 *M* KOH (about 14 ml), add 2 ml 13% TAA, and warm on a water bath with occasional stirring, until the sulfide-hydroxide precipitate has coagulated. Antimony will remain in solution as SbS_3^{3-}. If a colloid persists, add NH_4Cl and heat. Stir well, cool, centrifuge, and discard the precipitate.

ELUTION SCHEDULE FOR COLUMN B

(AG1-X10, 200-400 mesh, 0.79x14.9 cm, v = 7.3 ml, flow rate ~0.6 cm/min)

Volume							
ml	V	V_{50}	V_{99}	Reagent	Species Eluted	Disposition	Notes Fig.#
~100 15+15	~14 2+2			Load (4 *M* HCl; H_2SO_3) Wash (4 *M* HCl)	Rb,Cs,Na,As,(W) SO_2,HSO_4^-,*Ge,Fe*	Cs,Rb, pur.	b a
36	5		<2	0.3 *M* HCl	Ga, Mo	Discard	c
44	6	2.4	2.8	0.3 *M* HCl-1 *M* HF	Sb	Sb pur.	d 8
22	3			0.3 *M* HCl	HF	Discard	
44	6			0.5 *M* LiOH-0.5 *M* LiCl	Sn, (W)	Sn pur.	e 9
15	2			H_2O	LiOH-LiCl	Discard	a
44	6			0.2 *M* $HClO_4$	Cl,*Ir,Fe,Sb,Sn*	Save	f
22	3	~1.4		2 *M* $HClO_4$	ReO_4^-	Re pur.	g 11

(a) Rinse reservoir before adding eluent.

(b) A tracer experiment showed 0.06% of the Sb and 0.03% of the Sn in this fraction.

(c) 0.03% of Sn is in this fraction.

(d) 0.053% of Sn is in this fraction.

(e) 99.8% of Sn appears in this fraction. Li^+ is used instead of Na^+, to prevent interference by Na^{24} when reactivation is used to determine the chemical yield. Sn can also be eluted with 14V of 2 M HCl-3 M HF (Fig. 10), but is hard to recover from that medium.

(f) ReO_4^- has D_v = 10 in 0.2 M $HClO_4$, and hence should not elute in this fraction, especially since the first ~7v of $HClO_4$ serve to displace Cl^- from the resin, and ReO_4^- normally trails the ClO_4^- front. However, the initial loading was done from a large volume (~14v), from a medium in which ReO_4^- has a rather small D_v (~80, assuming total [Cl^-] = 5 M). Thus the ReO_4^- band probably is very broad, and may elute prematurely. The pre-Re fraction should therefore be saved until the Re fraction has been checked.

(g) With a 4.3 ml column, the Re fraction is only 13 ml, and hence can be acidified to 8 M (for Re_2S_7 precipitation), without exceeding the capacity of a 40 ml centrifuge tube. However, in view of the large volume of load solution, it seems safer to use a 7.3 ml column.

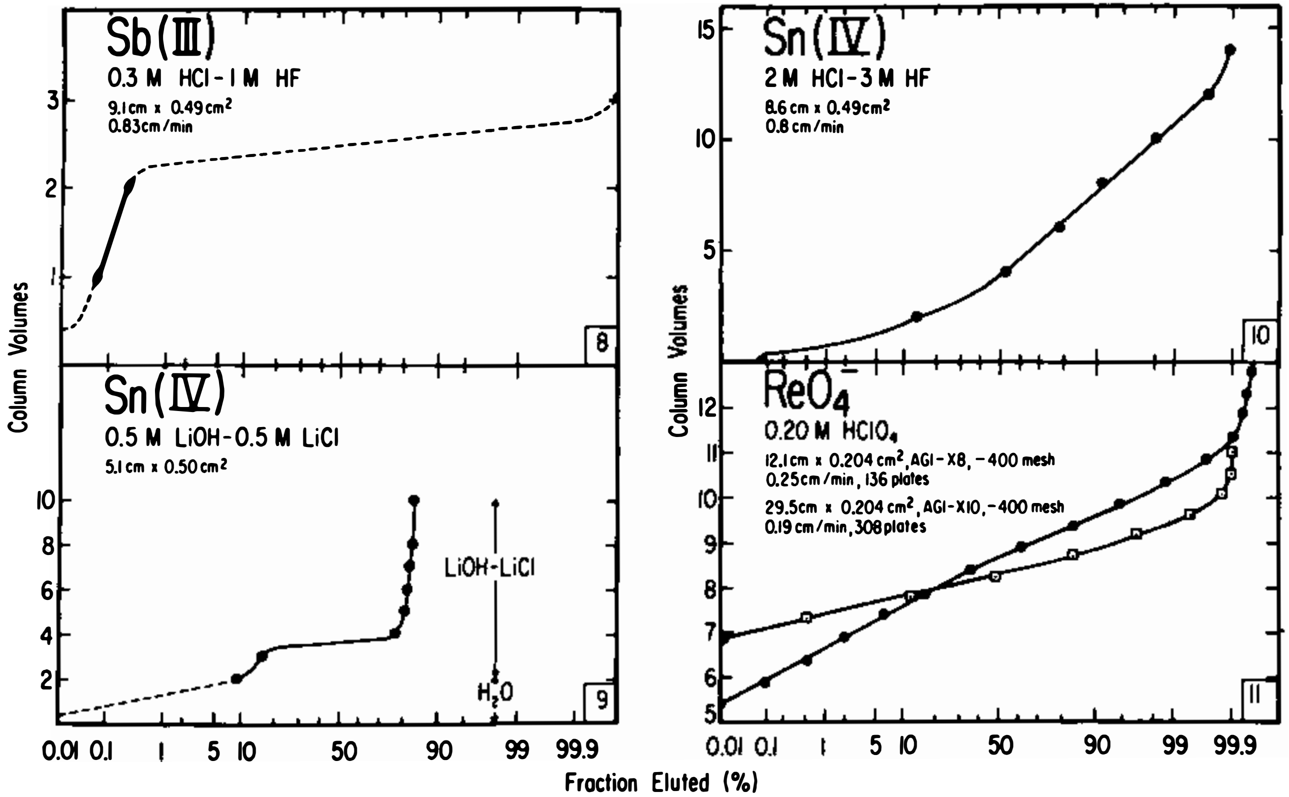


Figure 8-10. Elution curves of Sb and Sn from Bio Rad AG1-X10, 200-400 mesh anion exchange resin. For Sn, LiOH-LiCl gives smaller volume (though at the expense of lower yields), permitting direct measurement on a Ge(Li) detector.

Figure 11. Elution curves of ReO$_4^-$ (from Anders *et al.*, 1959). Both curves are sharper than those attained by the present procedure, due to the use of finer resin, thinner columns, and slower flow rates, but the curve for the 12 cm column should be fairly representative.

3) Transfer the SbS_3^{3-} solution to a 100 ml plastic beaker, and acidify to 1 *M* HCl by cautiously adding ~17 ml of 6 *M* HCl. Approach the neutral point (~5 ml HCl) dropwise, so that H_2S release does not get out of control. Decant the clear supernatant as far as possible, transfer the remaining liquid and Sb_2S_3 precipitate to a centrifuge tube, and wash the precipitate 2-3 times with 1 *M* HCl containing a drop of Na_2S.

Steps 2 and 3 can be carried out in 50 ml plastic centrifuge tubes if the Sb fraction is eluted in 2 installments: 3 to 3.5 v containing 99.99+% of the Sb (Fig. 8), and 2.5 to 3v for the remaining traces that could otherwise contaminate subsequent fractions. Alternatively, the solution in step 1 could have been evaporated to a smaller volume, with a corresponding reduction in the volumes of HCl and KOH added. Lastly, Sb_2S_3 can be precipitated directly from the HCl-HF solution after raising [HCl] to 1 M and adding the same carriers as in step 2. The sulfide precipitate is then treated with 0.5 M KOH, as in step 2. This variant gets rid of the fluoride early and also reduces the volume, but probably gives somewhat less effective decontamination than the sulfide precipitation in basic solution, outlined in step 2.

4) Add 8 ml 6 *M* HCl and heat to dissolve the precipitate. (Sb_2S_3 dissolves in hot 6 *M* HCl; if it doesn't, the acid may have become diluted by H_2O in the precipitate. In that case, add 1 ml concentrated HCl and continue heating.) After the solution has become clear and colorless, add 1 mg each of Zn^{2+}, Cr^{3+}, Fe^{3+}, and La^{3+} holdback carriers. Digest for a few minutes to expel H_2S, and filter or centrifuge if necessary. Discard any precipitate remaining (S, CuS, As_2S_3, Te, etc.). Wash the filter with 10 ml 2 *M* HCl.

5) Add 10 ml of $CrCl_2$ solution to the filtrate; metallic Sb precipitates. (If steps 2-4 have been skipped, do the precipitation in a plastic centrifuge tube, and wash twice with 1 *M* HCl before filtering, to remove HF).

6) Filter onto a glass fiber disk and wash with 1 *M* HCl, H_2O and methanol. Dry at 100°C. Allow 2.8 day Sb^{122} to decay before counting. Mount between doublesided scotch tape.

Average Yield: 60±15%.

Bismuth

The Bi abundances in lunar rocks and many meteorites are very low, resulting in activities as low as a few dpm. Thus decontamination factors from the major activities must be >10^{10}, especially since Bi^{210} is measured by β-counting. It is advisable to do the Bi purification in a separate, low-level lab, with special glassware (preferably new for the last few steps).

The procedure given here achieves the decontamination mainly by 3 ion-exchange separations. The most tenacious contaminants are Pa (which is well-behaved in the presence of F^-) and Ir (which tends to spread all over the place, cf. Column A).

1) To the 94 ml Bi fraction in 1 *M* H_2SO_4 add 1 mg each of Cr, Fe, Ir and Sb holdbacks, 1 ml saturated H_2SO_3 [to reduce Sb(V)) to Sb(III)], 8 ml HCl, to make [Cl^-] = 1 *M*, and ~20 drops 10 *M* HF, to complex Pa.

2) Load the solution on to a plastic anion exchange column: AG1-X10, 200-400 mesh, Cl^- form, 5.1 x 0.79 cm (v = 2.5 ml), with dacron fiber plugs; conditioned with 20 ml 1 *M* HCl. Elute according to the table below, at a flow rate of <2.5 cm/min. Use plastic receivers for all fractions containing fluoride.

A somewhat similar elution sequence on a 1 x 9 cm column gave the following decontamination factors: Fe 3 x 10^4, Ir ~500, Pa ~1000. An elution curve for Bi on a 1 x 10 cm column is shown in Fig. 6.

Volume		Reagent	Species Eluted	Disposition	Notes
ml	v				
104	42	Load (1 *M* HCl, 1 *M* H_2SO_4 0.1 *M* HF)	Fe,Cr,Co,Cu,Pa,Ir	Discard	
15	6	0.3 *M* HCl-1 *M* HF	Sb,*Fe,Pa*,(Ir?)	Discard	a
35	14	6 *M* HCl	Ir,F^-	Discard	a
35	14	0.001 *M* HCl	Zn,Cd	Discard	a,b
5	2	1 *M* H_2SO_4	Cl^-	Discard	c
30	12	1 *M* H_2SO_4	Bi	Step 3	d

(a) Thoroughly rinse reservoir before adding eluent.
(b) A white band of BiOCl forms on the column at this stage.
(c) This fraction, containing most of the Cl^-*, is being collected separately, because* Cl^- *inhibits the adsorption of Bi in the next, cation exchange step. From the information available, the cut at 2 v should remove >90% of the* Cl^- *while losing ≤1% of the Bi, but this has not been checked.*
(d) A tracer run on a 10 cm x 1 cm column (with 1 M H_2SO_4*-0.003 M HCl) and a flow rate of 0.9 cm/min gave* $V_{50} = 6v$*,* $V_{99} = 9v$*, so a cut at 12 v should be ample. However, because the present column is shorter and is being operated at a faster flow rate, it may be prudent to elute another 4 v with* H_2SO_4*, and to check an aliquot for Bi, using* Na_2S *or TAA.*

3) Dilute the Bi fraction from the anion exchange column (30 ml 1 *M* H_2SO_4) with twice its volume of water, to make $[H_2SO_4] = 0.33$ *M*.

4) Load the solution on a cation exchange column [1 x 5 cm (v = 3.9 ml), AG50W-X12, 200-400 mesh, H^+ form; conditioned with water and 0.25 *M* H_2SO_4]. Elute as follows:

Volume		Reagent	Species Eluted	Disposition	Notes
ml	v				
90	23	Load (0.33 *M* H_2SO_4)	Ir, anions	Discard	
58	15	Wash (0.25 *M* H_2SO_4)	Ir, anions	Discard	a
8	2	H_2O	H_2SO_4	Discard	a
20	5	0.5 *M* HCl	Bi	Step 5	

(a) Thoroughly rinse reservoir before adding eluent.

Bi^{3+} has the following distribution coefficients on AG50W-X8. H_2SO_4: 1 M = 32.3, 0.5 M = 235, 0.25 M = 6800. HCl: 0.5 M <0.5 (Strelow et al., 1965). The values for 12% crosslinked resin should be slightly larger (except for the HCl medium, where Bi is entirely anionic).

5) To the 20 ml Bi fraction in 0.5 *M* HCl add 2 ml 6 *M* HCl, to make $[Cl^-]$ = 1 *M*, and 4-5 drops 10 *M* HF.

6) Repeat step 2 (anion exchange column), but elute the pre-Bi and Bi-fractions (2 v + 12 v) together.

7) Add 2 ml of 13% TAA to the 35 ml Bi fraction and digest 10 min. on a hot plate. Centrifuge the Bi_2S_3 precipitate and reject supernate. Wash the precipitate with H_2O and reject washings.

8) Dissolve Bi_2S_3 in 1-2 ml HCl (1-2 drops of HNO_3 may assist). Boil off the H_2S. Reduce the volume to 0.5 ml and precipitate BiOCl by addition of water. Centrifuge and reject the supernate.

9) Dissolve BiOCl in 10 ml 2 *M* HCl. Dilute to 15 ml with H_2O, heat and add 10 mg Ag carrier. Allow to cool, and centrifuge. Filter the supernate into a new centrifuge tube. Discard the AgCl precipitate.

10) Add NH_4OH to precipitate $Bi(OH)_3$, centrifuge, and discard the supernate.

11) Dissolve the $Bi(OH)_3$ precipitate in 1 ml 6 *M* HCl. Add H_2O until the first turbidity appears. Allow to stand. Add H_2O from time to time until precipitation of BiOCl is complete.

12) Filter BiOCl onto a paper filter disk (lower background than fiber glass filter) and wash with H_2O and methanol. Dry in an oven at 110°C and weigh.

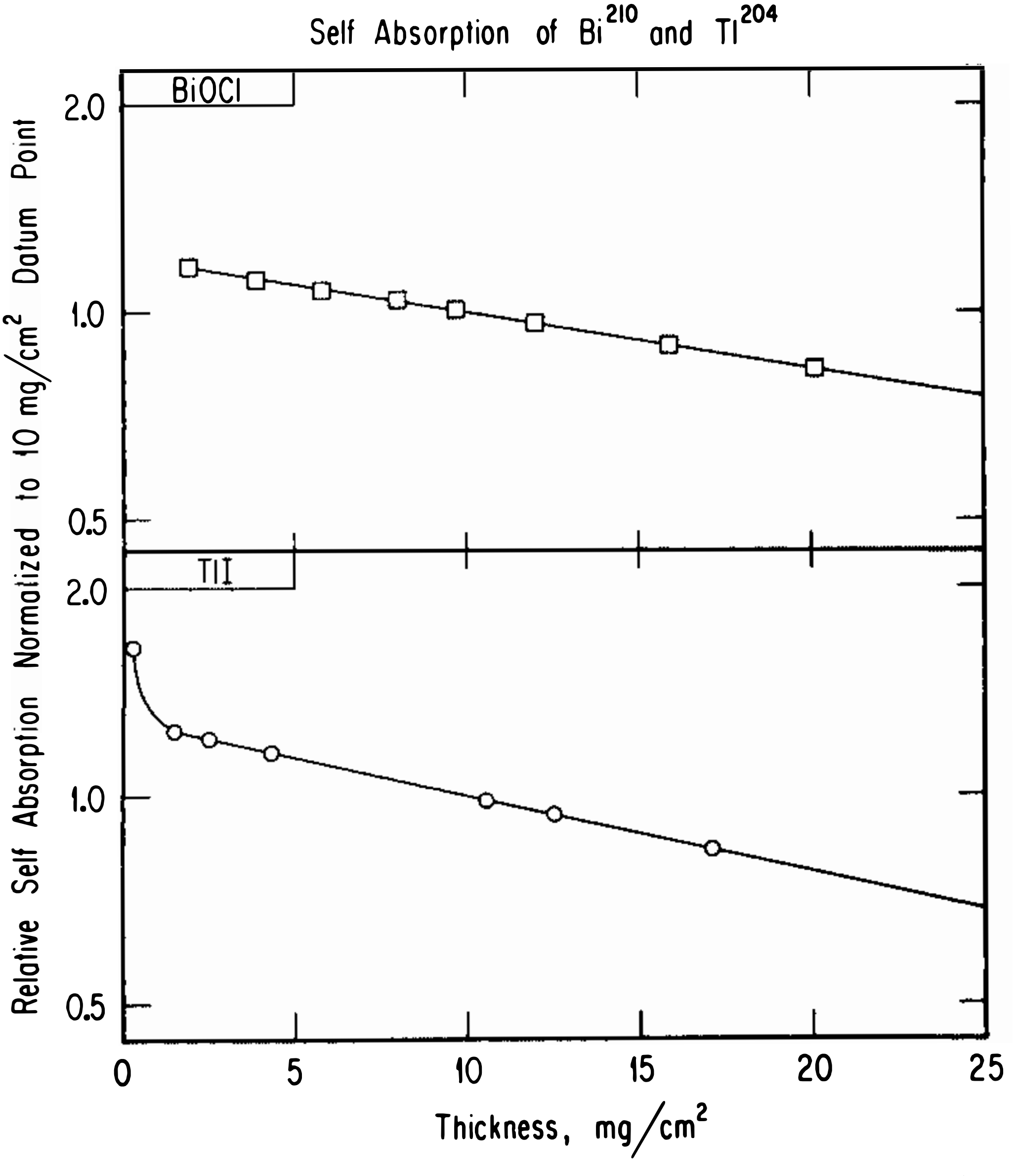


Figure 12. Beta self absorption for Bi^{210} in BiOCl and for Tl^{204} in TlI. Recalculated from curves given by Laul (1969), using a source area of 3.08 cm^2 (Laul *et al.*, 1970a). The data were arbitrarily normalized to a source thickness of 10 mg cm^{-2}.

13) Mount on a low background stainless steel disk and cover with mylar film. Count the Bi^{210} beta activity in a low background (~0.2 cpm) beta proportional counter. Correct activity for self-absorption (Fig. 12).

Average Yield: 47±6%.

Bromine

1) To the Br fraction from the Ge-Br separation (20 ml ≥0.05 *M* $NaHSO_3$) add 3 ml 3 *M* H_3PO_4 (to give final conc. ≈ 0.3 *M* H_3PO_4) and sufficient 0.2 *M* $KMnO_4$ (~3 ml) until all HSO_3^- and Br^- are oxidized, and the purple color of MnO_4^- persists.

2) Extract the Br_2 with two 20 ml portions of CCl_4 (D= 25). Wash the combined organic extract with 10 ml H_2O to remove Cl^-. Discard the aqueous layer.

3) Back extract Br into 15 ml freshly prepared 0.05 *M* $NaHSO_3$. Dropwise add more 1 *M* $NaHSO_3$ if the organic layer is not completely decolorized.

4) Make the Br fraction (15 ml) 3 *M* in HNO_3. Heat for 10 min (~80°C) to oxidize HSO_3^-. *A fuchsin test may be run to check for absence of* HSO_3^-*, although the test is not sensitive enough to indicate small amounts of* HSO_3^-.

5) Add 2 ml of 0.2 *M* $AgNO_3$ and check for completeness of precipitation. [Avoid an excess, else Ag_2SO_4 ($K_{sp} = 1.24 \times 10^{-5}$) may precipitate]. Digest for ~1 min, filter onto a fiberglass filter, and wash 3 times with water and 3 times with acetone. Dry for 30 min at 100°C. (If there is any chance that the samples have to be reirradiated, then filter paper should be used instead of fiberglass).

In the Keays et al. (1974) procedure, it happened occasionally that the AgBr ppt was heavier than expected, requiring the chemical yield to be determined by reirradiation. The likely reasons are:

i) Contamination with AgCl, if Cl^- was not scrupulously removed in earlier stages. (MnO_4^- slowly oxidizes Cl^- to Cl_2, which is extracted along with Br_2 and thus gets into the final sample).

ii) Coprecipitation of Ag_2SO_4. Some $SO_4^=$ is unavoidably formed by oxidation of HSO_3^-, and more may be introduced from H_2SO_4 used in the old procedure (the single extraction specified may not have removed it quantitatively). For this reason, avoid an excess of Ag^+ and keep $[H^+]$ fairly high (3 M), to tie up $SO_4^=$ as HSO_4^-.

iii) Coprecipitation of Ag_2SO_3. This is not likely to have happened, as $[SO_3^=]$ is very low in the strongly acidic (1.5-3 M) HNO_3 solutions used for precipitation. Moreover, if the solution was heated sufficiently, HSO_3^- would be oxidized to $SO_4^=$.

iv) Reduction of Ag^+ to Ag by HSO_3^-. This can happen, but the dark color of the precipitate is a clear warning that is hard to overlook.

Cadmium

1) To the 132 ml Cd fraction, add 1 mg each of Fe^{3+}, Zn^{2+}, Cr^{3+}, Sc^{3+}, and Co^{2+} holdback carriers. Add 6 ml HCl (to make [HCl] = 0.5 *M*). Add 5 ml saturated H_2SO_3 to reduce Fe^{3+} to Fe^{2+}.

2) Prepare an anion exchange column 1 x 5 cm, using Bio-Rad AG 1-X10 resin, 200-400 mesh, Cl^- form (nominal $\underline{v}$ = 3.9 cm^3). Condition the column with 30 ml of 0.5 *M* HCl.

3) Load the solution from step 1 onto the column (D_v of Cd = 2000). Adjust the flow rate to no more than 2.5 cm/min (even 1 cm/min if you have the time). Discard effluent, which should contain cationic species such as Co^{2+} and much of the Fe^{3+}, Cr^{3+}, Sc^{3+}. Thoroughly wash column reservoir. Elute as follows:

Volume ml	v	Reagent	Species Eluted	Disposition	Notes
138	35	Load (0.5 *M* HCl)	Fe,Cr,Sc,Co	Discard	
31	8	0.03 *M* HCl	Zn	Discard	Rinse reservoir
62	16	0.002 *M* HCl	Cd	Step 4	Rinse reservoir

4) Check γ-activity of Cd fraction. If Fe^{59} is present, do a $Fe(OH)_3$ scavenge with excess NH_4OH, evaporate to dryness, and take up residue in 50 ml 0.002 *M* HCl. If Fe^{59} is absent, proceed to step 5.

5) Add 5 ml 3 *M* NH_4Cl. Heat the solution to just below boiling, and precipitate $CdNH_4PO_4 \cdot H_2O$ by dropwise addition of 10 ml 1 *M* $(NH_4)_2HPO_4$. Check pH (should be at least 3-3.5) and adjust with a few drops of 0.1 *M* NH_4OH, if necessary. Continue heating until the precipitate becomes crystalline, and then allow to stand for 1-4 hours.

According to Wilson and Wilson, the best pH range for precipitation is 5.8-7.3, with the optimum at 6.5. However, in our experience, precipitation at so high a pH gives a fine, poorly filterable precipitate, and we therefore prefer to start with a weakly acid solution, relying on the $(NH_4)_2HPO_4$ *to raise the pH. Miller and Page (1901) recommend precipitating at room temperature and letting the solution stand overnight without any heating whatever, to prevent loss of* NH_3 *and* H_2O.

6) Filter onto a glass fiber disk. Wash with H_2O and acetone. Dry at 100-103°C. Mount on doublesided scotch tape and cover with mylar film.

7) Allow the 4.5 hour In^{115m} daughter to come to secular equilibrium with 54 hr Cd^{115} before counting.

Wilson and Wilson recommend 2-(o-hydroxyphenyl)-benzoxazole as a highly selective precipitant for Cd. (Only Cu, Co, Ni are precipitated by this reagent, but they are removed by the anion exchange.)

Average yield: 85±10%.

Cesium and Rubidium

1. Precipitation

If W is to be included in the procedure, then step C.5 must be used in place of step 1, below.

(1) Evaporate the Rb-Cs fraction from Column B to dryness. Toward the end of the evaporation, after the SO_2 is gone, add 10 mg of Fe^{3+} carrier. If the yellow color fades after addition of Fe^{3+}, add a few drops conc. HNO_3 to reoxidize iron to the +3 state, and continue the evaporation. Thoroughly leach the residue with 70 ml of water. Ignoring any turbidity, add 2 *M* Na_2CO_3, a few drops at a time. Centrifuge and discard the $Fe(OH)_3$ precipitate, containing Si, Ti, Al, Ca, etc.

(2) To the clear supernate (filter if necessary) add a few drops methyl orange, 3 ml 1 *M* sodium acetate, and glacial (17 *M*) acetic acid, one ml at a time, until the indicator begins to change from yellow to red.

The final pH should be between 3 and 5, preferably near the pK_a *of methyl orange (3.7). The pH of the acetate buffer system is 4.75-log HAc/NaAc.*

(3) Gradually add, with stirring, 20 ml 0.1 *M* (3.42%) sodium tetraphenyl borate ($NaB\Phi_4$) solution. Check for completeness of precipitation, and add more reagent if necessary. Cool to ≤20°C, and centrifuge as soon as possible after precipitation (less than 1 hr). If the precipitate does not settle, add 10 drops of 0.1 *M* $AlCl_3$ solution.

(4) Wash 2-3 times with 30 ml of a freshly prepared solution 0.003 *M* in $NaB\Phi_4$ and 0.1 *M* in HAc (30 ml 0.1 *M* $NaB\Phi_4$ and 6 ml glacial acetic acid per liter). The precipitate ought to be clean enough for counting, in solid or liquid form.

__Note__. A variety of contradictory statements on this reagent exist in the literature (see Wilson and Wilson, pp. 28-30, for a review, and Geilmann and Gebauhr 1953, for a most detailed study of precipitation conditions). The following salient facts have been extracted from the references given in Wilson and Wilson, and Kolthoff and Elving.

(a) The reagent is unstable in solution. Though some authors claim stability for 1-2 days (especially at 0°C or when dissolved in 0.01 M NaOH rather than H_2O), it should be freshly prepared and refrigerated until ready for use. For gravimetric work, the slightly turbid solution is usually cleared by shaking with alkali-free $Al(OH)_3$ and filtering, but this does not seem necessary here.

(b) The best pH range for precipitation is 3-6.5. Higher acidities, to $[H^+] = 0.66$ M, give a coarser precipitate and better selectivity (separation from Fe, Al, etc.), but the reagent decomposes rapidly at pH <3, yielding non-stoichiometric precipitates and requiring carefully controlled conditions (0°C, filtration in less than 10 min, larger excess of reagent). Reaction conditions, effects of other ions, etc. have been studied much less thoroughly for strongly acidic than for weakly acidic solutions.

Because Fe, Al, and other hydroxides are eliminated before the precipitation of Rb and Cs, low pH has no advantage, except coarser grain size of the precipitate. Filterable precipitates can be obtained at higher pH, however, by slow precipitation (at 40-50°C, if necessary) and addition of $AlCl_3$. Dropwise addition of reagent is supposed to be most effective.

(c) Though the solubility products of $RbB\Phi_4$ and $CsB\Phi_4$ are fairly small (2.0×10^{-9} and 8.4×10^{-10}), appreciable losses will occur unless excess $B\Phi_4^-$ is present in the solution as well as the wash liquid. The concentrations used here, 0.01 M (allowing for up to 2% K in a 0.1 g rock sample) and 0.003 M, should lead to a loss of only 1.9 μg Rb in the precipitation and 5.1 μg Rb in the washing, and slightly smaller losses for Cs. These calculated solubilities have been confirmed by Geilman and Gebauhr under actual experimental conditions. Solubilities in pure water are considerably higher (obs. 344 μg Rb/100 ml, calc. 382 μg/100 ml).

The procedure still works well in the presence of large amounts of NaCl or Na_2SO_4 (to at least 150 g/l or 100 g/l, respectively, corresponding to molar ratios of 600-1000), but the precipitate then contains a few percent of Na. The Na can be eliminated by dissolving the precipitate in acetone and reprecipitating by addition of water. Alkaline earths are slightly coprecipitated even at molar ratios of 1, but are eliminated in our procedure by precipitation with Na_2CO_3.

2. Preparation for Counting

Solid. Centrifuge, slurry with 0.5 ml of water, transfer to a planchet or vial, and dry. Be sure geometry and sample thickness are nearly the same for all samples; this is essential for counts in close geometry. If they differ appreciably, count the samples in liquid form.

Liquid. Transfer the precipitate to a 150 ml beaker, add 25 ml 4 *M* HNO_3, and heat overnight. Add 2 ml 70% $HClO_4$ and digest until the solution is a clear yellow or colorless. Evaporate the solution to 15 ml, and transfer to a 7 x 2 cm counting vial.

Note. This procedure, from Keays et al. (1974) may be too drastic and time-consuming. In acid solution, tetraphenylborates hydrolyze according to the equations:

$$KB(C_6H_5)_4 + HCl \rightarrow (C_6H_5)_3B + KCl + C_6H_6$$

$$(C_6H_5)_3B + 2H_2O \rightarrow (C_6H_5)B(OH)_2 + 2C_6H_6$$

Evaporation with 6 M HCl alone may suffice to complete the hydrolysis and to boil off the benzene; if a precipitate remains, it can be discarded, because it should contain no alkalis.

Counting. Count on a well-shielded Ge(Li) detector. Put samples in lucite sample holder directly on the detector. Usually, two counts are taken: first, a short count (400 sec) for Cs^{137} (662 keV) to determine the yield; second, a longer count (4-24 hours) for Cs^{134} (795.8 + 801.9 keV) and Rb^{86} (1085 keV), with the lower discriminator at such a value that the 662 keV γ-ray of Cs^{137} is not recorded.

Notes. Check each batch of tracer solution for Cs^{134} activity and correct for this contribution if necessary.

Some Cs^{137} is produced by fission of U^{235} in the sample. For typical irradiation and counting conditions even as much as 1 μg U produces only 1 cpm Cs^{137}, which is completely swamped by 2.10^3 cpm Cs^{137} added as tracer.

The above procedure assumes that Rb and Cs do not fractionate during the separation, so that the Cs yield also applies to Rb. This is true when the tetraphenylborates are quantitatively precipitated, and do not decompose in subsequent processing. However, when precipitation is incomplete (most commonly due to decomposition of reagent), then Rb is lost preferentially. For chemists unfamiliar with the procedure, it is advisable to check Rb yields by re-irradiation until the data consistently agree with the Cs^{137} yield.

Average yield: 61±10%.

Germanium

Having gone through a distillation, CCl_4 extraction, and a sulfide precipitation, the samples are clean enough for counting, and merely need to be filtered and mounted according to step 1, below.

If further decontamination from As is required, a second distillation can be carried out; alternatively, the following procedure may be convenient.

i) Dissolve the GeS_2 precipitate in 5 ml NH_4OH, centrifuge, remove supernate, and treat the residue with a second 5 ml NH_4OH portion. Centrifuge and combine supernate; discard residue.

ii) Add 10 ml NH_4OH to combined supernate, filter through a Whatman 41 ashless paper, and evaporate the filtrate to dryness on a water bath. Redissolve in 15 ml 4 M HCl to yield a clear solution.

iii) Add 1 ml As carrier and 0.5 ml 1 M NaI (to reduce any As(V) to As(III) and warm on a water bath. Transfer the solution to a polypropylene centrifuge tube and add 0.5 ml 10 M HF to complex Ge. Saturate with H_2S to precipitate As_2S_3.

iv) Centrifuge and filter through a Whatman 41 ashless paper into a glass centrifuge tube containing 5 ml saturated H_3BO_3 solution (to tie up F^-). Saturate with H_2S and store in a refrigerator. Continue with step 1, below:

1) After allowing the samples to stand for 24 hours, filter onto a paper disk. Wash with H_2O, trying to get the precipitate evenly distributed over the filter. Dry at 105°C; any sulfur in the precipitate will slowly volatilize. Mount on scotch tape only (or stiff, 10-mil mylar) and cover with scotch tape. Count the 9.3 keV Ga K X-ray of 11.4 d Ge^{71}, using a Si(Li) high-resolution, low background detector. Take great care to keep the geometry reproducible.

Determine the chemical yield by re-irradiation.

Re-irradiation. Prepare 4 monitors for the re-irradiation by weighing ~20 and ~50 mg of $(NH_4)_2\ Ge(C_2O_4)_3 \cdot 4H_2O$ in a plastic glove finger. Mount on cards and cover with scotch tape.

Note that the exact mass of the Ge in the samples need not be known, except for the self-absorption correction, because we use the ratio of the chemical yields of the samples to the chemical yields of the standards.

1) Wrap samples (12), standards (A+B), and monitors (4) together in Al-foil and place them in the can for a 10-min irradiation.

2) After irradiation, mount each of them on an Al plate, and cover with tape. (Alternatively, the samples can be sandwiched between two layers of tape or put into plastic vials, but the shape and spacing must be constant enough so that all samples have the same counting efficiency when counted in close geometry in step 3b.)

3) Count on a Ge(Li) detector at the appropriate distance, using a sample holder. The most intense peak is the 264.0 keV γ-peak of 82.8 min Ge^{75}, which has an interference from the 265.45 keV peak of 678 min Ge^{77}. Usually, two sets of counts are taken:

a) Shortly after irradiation, count the monitors and samples. If possible, repeat the cycle so that each of the samples is counted twice. Check that decay factor is consistent with half-life.

b) Count the samples again as close to the detector as possible and more than 15 h after the irradiation. Using this count for the isotope Ge^{77} only, 1 mg Ge can still be determined within 2% counting statistics. Check decay factor.

Average yield: 64±8%.

Gold

1) Make the Au fraction from Column A (94 ml 10% thiourea) about 1.5 *M* in NH_3 by adding 10 ml conc. NH_4OH. *(As the solution was acid to begin with, it will be buffered to pH 9-10 by the* NH_4^+ *salts formed.)* Heat to boiling, to hydrolyze thiourea, and precipitate Au_2S_3. Continue boiling until the dark-brown sulfide has coagulated. Decant, centrifuge, and wash the precipitate 2-3 times with 1 *M* HCl. Be sure to get rid of all organic matter on the walls.

2) Dissolve the precipitate in a few drops of aqua regia, add 10-20 ml 6 *M* HCl and 2 ml 5 *M* NaCl, and centrifuge. Discard the sulfur residue and transfer the supernatant to a 150 ml beaker.

It is advisable to get rid of the sulfur as completely as possible, because it may interfere in later steps. If the supernate is not completely clear, boil the solution to coagulate the sulfur.

3) Evaporate the solution to dryness. Moisten the residue with conc. HCl, and evaporate just to dryness; repeat twice to remove all traces of NO_3^-.

The NaCl aids in the removal of nitrate. If red specks of metallic Au appear at some stage (owing to reduction by S or organic matter), dissolve them with Cl_2*,* Br_2*, or a few drops* HNO_3*. (The latter two must be removed by 3 evaporations with 1-2 ml HCl).*

4) Take up the residue in 30 ml 1.2 *M* HCl. Heat to boiling, and slowly induce precipitation of Au by adding, a drop at a time, a 5% hydroquinone solution (the solution is stable for up to a week). After nucleation has commenced, add 5 ml of reagent, and continue to boil for 20 min.

If Pa is present, add 5 drops of 10 M HF before precipitation. Because HF attacks glass, if is preferable to do the reaction in a polypropylene beaker.

A single precipitation suffices because the Au fractions from Column A (eluted with neutral thiourea rather than 0.1 M HCl-thiourea) are >95% clean, with Fe^{59} *the only detectable contaminant.*

5) Filter onto a glass fiber disk, using a small (10 mm) chimney, and wash thoroughly with water. Use ethanol to transfer the precipitate quantitatively. Dry at 110°C. Mount the samples between double-sided scotch tape. Use antistatic spray on the mylar film (or breathe on it heavily!) before covering the Au precipitate.

Average yield: 84±13%.

Indium

1. Preliminary Purification of In and Ni

The initial purification of In and Ni is done simultaneously, on the same cation exchange column. The method involves elution with acetone-HCl mixtures of increasing acetone content (and hence decreasing dielectric constant). Cations of progressively lower affinities for Cl^- thus are able to change into anionic complexes that are promptly eluted from the column (Fritz and Rettig, 1962).

The In fraction from Column A tends to be contaminated with Ir^{192} and Cr^{51}, ($\tilde{}10^4$ c/m) and lesser amounts of Sc^{46} and Co^{60}. The $Ni(DMG)_2$ precipitate is contaminated mainly with Co^{60}, ($\tilde{}10^5$ c/m). Because Cr forms several inert Cl^- complexes that elute at different rates, the procedure includes conversion of Cl^- to NO_3^- and for most of our work a second ion exchange step in 5 M HCl on a long, thin column was used. It works well but takes too much time. Recently, a faster procedure has given good results (M. Ebihara, to be published). The second ion exchange step uses acetone-HCl instead of 5 M HCl. This alternative method will be outlined in sec., 2 on p. 60.

1) Dissolve the $Ni(DMG)_2$ precipitate (from B.6) in 1 ml HNO_3. Combine with the In fraction (94 ml 3.5 *M* HCl) from Column A, as well as 1 mg Fe, Cr, Co, Cd, Zn, Ir and La holdbacks, and 20 μg Sc holdback. Evaporate to near dryness and add sufficient HNO_3 to convert chlorides to nitrates. Evaporate to dryness on low heat (excessive heating produces a black oxide that is almost impossible to dissolve), and take up in 10 ml 0.1 *M* HNO_3. The solution should be light brown with no green color left.

2) Load the Ni-In solution on a 14.9 ml cation exchange column (AG50-X12, 200-400 mesh, 1x19 cm, H^+ form, conditioned with water until the pink color of resin impurity is gone, and then with 50 ml 0.1 *M* HNO_3). Wash with 30 ml 0.1 *M* HCl and elute according to the following table, at a flow rate of ≤0.5 cm/min. Cover the columns loosely with parafilm to prevent evaporation of acetone, but pierce a small hole so a vacuum won't form.

Volume ml	v	Reagent	Species Eluted	Disposition	Notes
10	0.7	Load (0.1 *M* HNO$_3$)	} Ir, anions	Discard	a
30	2	Wash (0.1 *M* HCl)			b,c
45	3	40%A-0.5 *M* HCl	In, Cd	In pur.	d,e
90	6	90%A-0.5 *M* HCl	Fe,Co,Zn	Discard	f
30	2	3 *M* HCl	Ni	Ni pur.	g

(a) The ions adsorb according to charge and size: green Cr^{3+} at the top, colorless In^{3+} in the middle, blue Co^{2+} and green Ni^{2+} at the bottom.

(b) Thoroughly wash reservoir before adding eluent.

(c) Check γ activity of adsorption band, and continue washing with 2 v increments of 0.1 M HCl until activity has become negligible or constant.

(d) Because a tracer experiment indicated that 0.2% of the Cd appears in the In fraction from column A, one can insert an elution step for Cd at this point: 1.8 v of 70%A-0.2 M HCl (Fritz and Rettig, 1962). However, this step has not been tested, and may not be worth the trouble if In is purified by another anion exchange later on.

(e) Fritz and Rettig use only 2.5 v to elute In quantitatively, but since they start with resin already pre-equilibrated with acetone, it seems safer to use 3 v, which gives good yields.

(f) According to literature data, 3.2 v suffices to elute Co, the most strongly adsorbed of these 3 ions, to 99.8%. However, because Co^{60} and Fe^{59} are the major contaminants, it may be worthwhile to continue the elution with additional 2 v increments until the point of diminishing returns has been reached. D_v *of Ni in this medium is 249, so there is not much danger of eluting it prematurely.*

(g) The elution of Ni can be followed by watching the green Ni band. Typically, Ni emerges in the interval 0.7-2v (10-25 ml), and it may therefore be worthwhile to collect a separate pre-Ni fraction of about 10 ml, to see whether a significant amount of contamination can be removed this way. The trailing edge of the Ni band is less sharp than the leading edge, and the elution should therefore be continued until a drop of effluent no longer gives a DMG test for Ni. It is advisable to stop shortly after the Ni band has fully emerged, because the heavy REE will soon follow. For example, D_v *for Ni and Yb are 2.0 and 12.2 in 3 M HCl and 7.2 and 27.4 in 2 M HCl. If desired, the elution can be done in 2 M HCl, though the separation should be amply good enough in 3 M HCl.*

Fritz and Rettig (1962) suggest loading no more than 1.5 meq. on a 14 ml column to minimize tailing, so one should really use a 21 ml column for 2.2 meq. of In, Ni, and holdbacks.

The notation "40%A - 0.5 M HCl" means a mixture of 400 ml acetone, 42 ml 12 M HCl, and 558 ml H_2O without regard to volume change on mixing. Similarly, 90%A - 0.5 M HCl is 900 ml acetone, 42 ml 12 M HCl, and 58 ml H_2O. The mixtures of high acetone content, at least, must be freshly prepared, because they turn dark owing to polymerization reactions.

Fritz and Rettig recommend that the column be prepared from and conditioned with the first eluent, and that the (neutral) loading solution should contain 50% acetone. This is probably important when the first eluent has a high acetone content, because the volume change in the sudden transition from aqueous to organic medium can cause channeling. However, since our first eluent has only 40% acetone, we can start in aqueous medium.

2. Purification of In

1) Add the following holdbacks to the In fraction from the cation exchange column: 1 mg each of Fe, Co, Cr, and La. Evaporate to dryness, and take up residue in the minimum volume (<5 ml) of 5 *M* HCl. Discard any purple residue of $CrCl_3$.

2) Load the solution on an anion-exchange column (0.69x15 cm, v = 5.6 ml; AG1-X10, 200-400 mesh, Cl^- form; conditioned with 20 ml 5 *M* HCl). Elute according to the table below, at a flow rate of <0.5 cm/min.

On such a column, In shows essentially the same elution behavior in 2-8 M HCl: $V_{50} = 6.5$ v, $V_1 = 5$ v, $V_{99} = 11$ v *(the latter is strongly dependent on the flow rate and resin mesh size). Tracer experiments with 2 M and 5 M HCl show that the latter gives better decontamination from contaminants surviving the cation exchange step (Fe, Co, Cr, Sc, Ir). Due to the small D, a long column and slow flow rate are needed.*

As a faster alternative, steps 1 and 2 may be replaced by the following procedure (M. Ebihara, to be published).

Evaporate to dryness the In fraction from the preceding cation exchange column, take up the residue in HCl and prepare for loading as 10 ml of 1 M HCl - 40% A solution. Load on a second cation-exchange column (1.0 x 7.5 cm, v = 5.9 ml; AG50-X12, 200-400 mesh, conditioned with H_2O to remove pink impurity, then 20 ml 1 M HCl - 40% A). Elute In with 15 ml (2.5 v) of 1 M HCl - 40% A mixture. Continue with step 3.

Volume ml	Volume v	Reagent	Species Eluted	Disposition	Notes
<6	<1	Load (5 *M* HCl)	Co, Cr, Mn, Sc, other cations	Discard	
5.5	1	Wash (5 *M* HCl)			Rinse reservoir
24	4.3	5 *M* HCl			
39	7	5 *M* HCl	In	Step 3	

3) Evaporate the In fraction to dryness, and take up in 10 ml 2 *M* HCl. Add 50 ml water and 17 ml 2 *M* sodium acetate. Check that the pH is between 4 and 5.

4) Heat the solution to 70-80°C. Dropwise add 8-hydroxyquinoline solution [5% (w/w) in 2 *M* acetic acid] until no further precipitation occurs. Wash the precipitate thrice with 10-15 ml warm (60-80°) water.

5) Quantitatively transfer the ppt into a weighed plastic vial (14 x 52 mm). Centrifuge the vial, discard the supernate, and dry the vial in an oven at 110°C for 2-3 hr. Cool and weigh. (One type of vial reproducibly lost 3.1±0.1 mg on drying at 110°C, and hence required a corresponding correction. A more heat-resistant plastic is preferable.)

6) Dissolve the In oxinate precipitate in a minimum, and constant, volume of 6 *M* HCl (e.g., 1.5 ml for precipitates of 100-400 mg). Count the 192 kev γ-ray of In^{114m} on a well crystal. Because the 1.99 MeV β's of In^{114m} penetrate the vial and crystal mount, a Cu insert (0.9 mm walls) should be used in the well, to absorb the β's.

Average yield: 62±13%.

Iridium

1) To the Ir fraction from Column A (115 ml 6 *M* HCl), add 1 mg each of the following holdbacks: Fe, Cr, La, Sc, and Ru. Evaporate to dryness, take up with 5-10 ml aqua regia, evaporate, take up with HCl and evaporate slowly to dryness. Repeat the HCl evaporation for a total of 3 times.

2) Add 10 ml of 0.03 *M* HCl and warm on a hot plate to dissolve the residue. Transfer to a 40 ml centrifuge tube, cool and centrifuge. Prepare a plastic cation-exchange column, 0.7 cm x 10 cm, using Bio-Rad AG50W-X12, 200-400 mesh, hydrogen form. Wash the column with H_2O until the effluent is colorless (initially it is orange-pink, from soluble impurities in the resin). Load the sample solution onto the column and collect the eluate. $IrCl_6^{-2}$ passes through the column while Cr^{3+}, Co^{2+}, and Fe^{3+} are retained. Wash the column with 0.03 *M* HCl until the eluate becomes colorless (≈5 ml).

3) Evaporate to 5-8 ml and transfer to a weighed 1-dram screw-top glass vial.

4) Make up to volume with 0.03 *M* HCl, mix well and reweigh. Take an aliquot of about 10% by weight for chemical yield determination by re-irradiation.

If the reactor position used for re-irradiation has a high epithermal neutron component, much of the Ir^{192} is produced by resonance absorption effects (Steinnes, 1971). Due to the high cross section and narrow energy width of the resonance absorption peaks, self-shielding then may become a significant problem. In such cases, a smaller aliquot should be taken (≈ 50 μl) and weighed, then absorbed on high purity SiO_2 and dried.

5) Count the 470 keV γ-ray of 70 d Ir^{192} on a Ge(Li) spectrometer.

The same radionuclide is used for the yield determination. A very small correction may be necessary for the original Ir^{192} activity in the aliquot before re-irradiation. (There is little advantage in using 17 hr Ir^{194}, because of its lower γ-branching ratio and production rate.)

Average yield: 74±12%.

Nickel

1) To the Ni fraction from the cation exchange column add 1 mg Fe, Co, and Mn carriers. Evaporate to dryness and take up the residue in 20 ml 0.5 *M* HCl.

2) Add 1 drop of H_2O_2 (3%) and 9 ml 1 *M* NH_4OH. Continue adding 1 *M* NH_4OH, dropwise, until $Fe(OH)_3$-MnO_2 begins to precipitate; then add 3 ml in excess so that $[NH_3] \approx 0.1$ *M*. The pH of this NH_4^+-NH_3 buffered solution is $9.25 - \log [NH_4^+]/[NH_3]$, and hence should be between 8 and 9. Centrifuge and discard the precipitate.

3) To the supernatant, add a few drops of Aerosol, 30 ml water, and 8 ml DMG (1% in 95% ethanol), to precipitate Ni. Heat at 60° for 30 min.

The stoichiometric amount of DMG solution is 5.8 ml. The total volume is raised to ~70 ml to prevent precipitation of excess DMG (solubility 0.4 mg/ml), and to minimize losses of $Ni(DMG)_2$ *(it is appreciably soluble at alcohol concentrations greater than 35%).*

Wilson and Wilson suggest precipitating at room temperature if Co is present (as it is here, because the Co holdback is now in the form of $Co(NH_3)_6^{3+}$*), and then heating at 60° for 30 min. They also recommend filtering the solution after it has cooled.*

4) Let cool, and filter through a fiberglass disk. Wash with ~50 ml water (40-60°C) containing a few drops of Aerosol, and then with methanol. Dry at 150°C, to volatilize any excess DMG. Mount over a 2.5 cm hole in a 5 cm dia. lucite ring to avoid backscattering from the lucite and cover with Scotch tape. Count the 7.5 kev Co Kα X-ray of 80,000 yr Ni^{59}, using a Si(Li) detector. Apply corrections for self-absorption and for Ni from the sample itself (this is significant at Ni contents >0.1%, e.g., chondrites).

Average yield: 69±5%.

Osmium

The osmium samples are purified by distillation in a still similar to that used for the initial separation, but equipped with an addition funnel controlled by a teflon stopcock.

1) Transfer the Os-containing NaOH solution to a 100 ml distilling flask and assemble the still. The receiver is a large test tube containing 20 ml freshly prepared 2% thiourea in 2 *M* HCl, cooled in an ice bath. Air is slowly bubbled through the still at a rate not exceeding 3 bubbles/sec.

At faster bubbling rates, OsO_4 *is not quantitatively absorbed by the receiver solution.*

2) Through the funnel, dropwise add 1:1 H_2SO_4 until neutral (as indicated by effervescence and decoloration). Add 5 ml 1:1 H_2SO_4 in excess and 5 ml 30% H_2O_2 solution.

3) Distill OsO_4 at 90°C for 30-60 min, while dropwise adding H_2O_2 to replace that decomposed by heating. The raspberry-red Os(III) thiourea complex forms in the receiver.

Some authors boil the solution (Westland and Beamish, 1954, 1957), whereas others merely heat at 90° (Crocket et al., 1968). The optimum initial temperature depends on transition element cations present in the solution that may catalyse the strongly exothermic decomposition of H_2O_2*. In the present case, the solution is free from these cations and little of the* H_2O_2 *decomposes to supply additional heat. Nevertheless, for radiochemical separations, lower temperatures may be preferable, because they cause less spray and mechanical carryover (*H_2O_2 *interferes with the thiourea reaction). However, the temperature must be high enough for efficient volatilization of* OsO_4 *in the particular apparatus used.*

4) Pour the colored thiourea solution into a 40 ml centrifuge tube (through a filter, if any particulate matter is present). Add 1 ml of a filtered 40% $K_3[Cr(SCN)_6]$ solution. Stir thoroughly for at least 5 min, scratching the tube with a glass stirring rod if necessary to initiate precipitation.

5) Filter the precipitate onto a glass fiber disk, wash with water and dry at 105°C. Weigh the $Os(NH_2\text{-}CS\text{-}NH_2)_6\ Cr(SCN)_6$ precipitate to determine the chemical yield (gravimetric factor = 0.1816).

6) Mount the filter onto scotch tape and cover with scotch tape. Count the 129.4-keV γ-ray of 15.4-d Os^{191} on a NaI(Tl)-detector.

Average yield: 56±17%.

Palladium

1) Precipitate PdI_2 in the Pd fraction from Column A by dropwise addition of 1 *M* KI, until the precipitation is complete (stoichiometric amount = 0.23 ml), and then 1 ml in excess. Centrifuge and wash twice with 1 *M* HCl. Discard the supernate.

Avoid an excess of more than 3 ml, because the precipitate is soluble in a larger excess of KI (Beamish and Dale, 1938). If Pa^{233} is present, the solution should be made 0.05 M in HF before precipitation.

2) Dissolve the precipitate in a few drops of aqua regia and evaporate to dryness. Remove nitrogen oxides by evaporation with 1-2 ml HCl. Take up the residue in 20 ml 0.5 *M* HCl.

It seems that small amounts of NO_3^- can be tolerated; Wilson and Wilson recommend making the solution 0.08-0.16 M in HNO_3 to prevent Pt from coprecipitating. A more important function of the evaporation is removal of I^-.

Kolthoff and Elving (p. 453) remove HNO_3 by adding formic acid to the hot (85°) solution until no more red vapors are formed. But since formate reduces Pd^{2+} to the metal on boiling, this step seems rather precarious.

3) Warm the solution to about 80°C on a water bath. Dropwise add dimethylglyoxime (1% in ethanol) until no more precipitate forms (about 4-5 ml should be required). Cool to room temperature.

4) Check the gross γ-activity of the precipitate on a 3"x3" NaI detector, with a threshold of 200 keV. It should be less than 30 cpm above background. If the activity is higher, repeat steps 2 and 3.

In one run where Ir (38,000 cpm) and Pa^{233} *were the main contaminants, the first* PdI_2 *precipitation gave a decontamination factor of ˜*10^3 *from Ir, but the second one only ˜5-10x from Ir and 2-5x from Pa. The DMG precipitation gave decontamination factors of ≥10x (probably much more, because the activity was quite low at that stage).*

5) Filter the precipitate in the center of a glass-fiber disk, and wash with 0.5 *M* HCl, water, and ethanol. Dry at 110°C. The chemical yield is determined by weighing the palladium dimethylglyoximate (gravimetric factor = 0.3161).

6) Mount the filter between 2 layers of scotch tape to provide a fixed geometry of the precipitate on the filter. Count the 20.2 keV Rh Kα x-ray of 17 d Pd^{103} on a small Ge-low-energy-photon-detector (LEPD).

Average yield: 62±13%.

Rhenium

1) To the Re fraction from Column B (22 ml 2 *M* $HClO_4$) add 16 ml HCl, to make $[H^+] = 6$ *M*, and 1 mg $FeCl_3$ and Ir holdbacks. Add 2 ml 13% TAA, stir well, and heat in water bath until the precipitate has coagulated (˜30 min). Centrifuge and wash twice with water.

Some authors suggest letting the mixture stand overnight at room temperature, but that does not seem necessary. In fact, the fast precipitation on a water bath seems to give a better yield.

2) Dissolve the Re_2S_7 precipitate in 3 ml 1 *M* NH_4OH and 1 ml 30% H_2O_2. Heat in a water bath until H_2O_2 has decomposed and the solution is colorless (indicating complete oxidation of sulfo salts); then evaporate to dryness.

Less than 3 ml NH_4OH *could be used because the excess has to be evaporated anyway, but the reaction may then get too vigorous.*

3) Take up the residue in ≤0.4 ml 0.2 *M* HCl and heat at 60-70° for 5 min. Load the solution on an anion exchange column [0.5 x 10 cm (v = 1.96 ml), AG1-X10, 200-400 mesh; ClO_4^- form, conditioned first with 20 ml 0.2 M

$HClO_4$, then with 10 ml 0.2 *M* HCl]. Wash the centrifuge tube with 2-3 0.2 ml portions of 0.2 *M* HCl, and transfer the washings to the column. Elute according to the following table.

The heating with HCl converts any Ir to $Ir(NO_2)_6{}^{3-}$, which is very weakly held by anion exchange resin. (The $NO_2{}^-$ needed for this reaction comes from oxidation of NH_3 by H_2O_2.) The volume of the load solution must be kept as small as possible, because $ReO_4{}^-$ has a small D_v on resin in the $ClO_4{}^-$ form, and hence tends to form very broad adsorption bands.

Volume		Reagent	Species Eluted	Disposition	Notes
ml	v				
0.4	0.2	Load (0.2 *M* HCl)	} Cations	} Discard	
0.8	0.4	Wash (0.2 *M* HCl)			
6	3	H_2O			a
9	4.5	0.20 *M* $HClO_4$	Fe, Ir	Save	b,c
20	10	0.20 *M* $HClO_4$	$ReO_4{}^-$	Step 4	Fig. 11

(a) Thoroughly rinse reservoir before adding eluent.
(b) The elution parameters for Re, based on longer columns of finer resin and slower flow rate, are V_1 = 6.5 - 7.5 v, V_{50} = 8.5 ± 0.3 v, V_{99} = 9.5 - 10.5 V (Fig. 11). The cuts for the present separation have been chosen somewhat conservatively.
(c) A similar column gave decontamination factors of $\geq 10^3$ for Fe and 50-100x for Ir (without conversion to NO_2^- complex).

4) To the Re fraction add 2 mg Fe^{3+} holdback carrier, and precipitate $Fe(OH)_3$ with a slight excess of NH_4OH. Heat, centrifuge, and discard precipitate. Filter if necessary.

5) Adjust acidity of supernatant to 4 *M* HCl, and add 2 ml 13% thioacetamide to precipitate Re_2S_7. Stir well and heat for 30 min, or let stand overnight. Centrifuge and discard the supernate.

6) Dissolve the Re_2S_7 precipitate in 3 ml 1 *M* NH_4OH and 1 ml 30% H_2O_2. Heat in a water bath until H_2O_2 has decomposed and the solution is colorless. Add sufficient NaCl solution to make the final [NaCl] = 0.5 *M*, and dilute to 10-15 ml. Filter off any sulfur present.

7) Add 2 ml of 0.05 *M* tetraphenyl arsonium chloride (Φ_4AsCl), drop by drop. Cool the mixture in an ice bath, and allow the Φ_4AsReO_4 precipitate to settle.

8) Filter onto a glass fiber disk and wash with ice cold water. Dry at 110°C.

9) Count the β^- activity of 90.6 hr Re^{186} on a low background β-proportional counter.

Average yield: 78±10%.

Silver

1) Wash the AgCl precipitate with 0.5 *M* HCl until the brown color of Ir disappears from the wash solution.

2) Add 20 ml 4 *M* NH_4OH, stir well and warm to dissolve the precipitate. Add 5 mg of Fe^{3+}, Co, Cr, and Ir carriers and heat to coagulate the precipitate. Centrifuge, filter supernatant into another centrifuge tube, and discard the residue. (If Ba analysis is required, $BaSO_4$ may be recovered almost quantitatively from this residue).

3) Add 1 mg Fe^{3+} holdback and 10 drops 2 *M* HCl, and acidify to 0.5 *M* HNO_3 with 6 *M* HNO_3, to reprecipitate AgCl. Centrifuge, wash twice with 0.1 *M* HCl, and discard the supernate and washings.

Because AgCl is fairly soluble at high [Cl^-], the solution is neutralized with HNO_3 rather than HCl and the washing is done with fairly dilute, 0.1 M HCl. The Fe^{3+} added in step 3 serves as a holdback upon acidification. Co, Cr, and Ir holdbacks should already be present in the NH_3 solution, because these elements were not precipitated in step 2.

4) Suspend the AgCl precipitate in 20 ml 1 *M* HCl, add 1 ml 13% thioacetamide, and heat to convert AgCl to black Ag_2S. Centrifuge, wash the precipitate once or twice with water, and discard supernate and washings.

5) Dissolve Ag_2S by heating with 1 ml of nitric acid. Add 20 ml of water, then filter into another centrifuge tube.

6) Add 5 mg of Fe, Co, Ir carriers and 10 drops of 2 *M* HCl to precipitate AgCl. Centrifuge and discard the supernate. Wash the precipitate.

7) Dissolve the AgCl precipitate in 20 ml of 4 *M* NH_4OH. Add 5 mg of Fe^{3+} carrier, stir well, warm, centrifuge, and filter into another centrifuge tube. Discard the $Fe(OH)_3$ precipitate.

8) Add 1 mg Fe^{3+} holdback [either $FeCl_3$ or $Fe(NO_3)_3$] and 10 drops 2 *M* HCl, and acidify to 0.5 *M* HNO_3 with 6 *M* HNO_3, to reprecipitate AgCl. Filter immediately onto a glass fiber disk. Wash with water until the wash liquid is neutral, then with acetone. Dry at 110°C. Mount between doublesided scotch tape.

Tellurium (+ Uranium) and Selenium

Two fractions are to be combined: the Te precipitate from Column A (B.5) and the Se, Te precipitate from the Ge distillation (C.3).

1. Separation of Se and Te

1) Combine the Te, Se precipitate from columns A and B, and wash it 1-2x with 4 *M* HCl containing some SO_2, $FeCl_3$, and Aerosol, and 2x with water, to remove Fe^{59} and Cs^{134} activities as well as HCl (else some Se may volatilize in the next step). Dissolve the precipitate in 3 to 5 ml HNO_3, and evaporate to near dryness on a waterbath.

2) Cool, add 5-10 ml 6 *M* HCl, and stir until residue is completely dissolved and the solution is a clear lemon yellow. Any sulfur residue may be filtered off. If the solution is still cloudy, it may be heated briefly. As soon as the sample has dissolved, proceed to step 3. *(Se must not stay in*

strong HCl any longer than necessary, because it slowly changes to another species of different properties.)

3) Load onto an anion exchange column [1.0 cm x 8 cm, (v = 6.3 ml), AG 1-X10, 200-400 mesh, chloride form; conditioned with 20 ml 6 *M* HCl]. (If the solution is not clear, filter through a hardened filter paper onto the column.) Elute according to the following table, at a flow rate of <1 cm/min.

Volume		Reagent	Species Eluted	Disposition	Notes
ml	v				
10	3.2	Load (6 *M* HCl)	Cations	Discard	a,b
5+5		Wash (6 *M* HCl)			
31	5	3 *M* HCl	**Se**	**Se** pur.	c
10	1.6	3 *M* HCl + 2 mg Se carrier	(Se)	Discard	d
38	6	3 *M* HCl	(Se)	Discard	
25	4	0.5 *M* HCl	**Te**	**Te** pur.	a,e

(a) Thoroughly rinse reservoir before adding eluent.
(b) A larger volume of wash solution would be desirable for more efficient removal of cations, but this step must first be checked with tracer. Se has a small and somewhat erratic K_D *in 6 M HCl, and may elute early.*
(c) The first 4 v should contain 99% of the Se [V_{95} *= 2 v(est.); V = 3-5 v (Schindewolf, 1960)].*
(d) The Se carrier must be free of HNO_3*. It helps remove traces of Se that otherwise cling to the resin and contaminate the Te fraction.*
(e) Check Te fraction on Ge(Li) detector and reprocess by step 4 if it still contains Se.

4) If the Te fraction still contains Se contamination, then it must be reprocessed by another anion exchange step. Add 2 mg Se holdback and 7 ml conc. HCl to the 25 ml Te fraction, to make it 3 *M* in HCl. Load on a 6.3 ml column (glass or plastic) and elute as follows:

Volume ml	Volume v	Reagent	Species Eluted	Disposition	Notes
32	5.2	Load (3 *M* HCl)	(Se)	Discard	
31	5	3 *M* HCl	(Se)	Discard	a
25	4	0.5 *M* HCl	Te	Te pur.	a,b

(a) Thoroughly rinse reservoir before adding eluent.
(b) Collect in centrifuge tube.

2. Purification of Te

5) Add 4 ml HCl to the Te fraction to adjust acidity to 2 *M* HCl, add 2 mg $FeCl_3$ holdback carrier [not $Fe[NO_3)_3$] and Aerosol, and pass SO_2 for at least 5 min.

6) Filter the Te precipitate onto a glass fiber disk, and wash with 2 *M* HCl containing SO_2 and a little $FeCl_3$ carrier, then with water and acetone. Dry at 110°C. Mount the precipitate in a scotch tape sandwich, but first cover it with an extra piece of 2 mil mylar, to permit remounting on an Al plate for β-γ coincidence counting, if necessary.

The purpose of the washing is to remove Fe, which is not separated from Te in the above ion exchange separation. The Fe holdback must be kept in the +2 state by excess SO_2, because Fe^{3+} reoxidizes and dissolves Te.

7) Count the 230 keV γ-ray of 78 hr Te^{132} (or the 668 keV γ-ray of its 2.3 hr I^{132} daughter) for the U determination. After a delay of 4 to 6 weeks to allow Te^{132} to decay, count the 159 keV γ-ray of 120 d Te^{123m} for the Te determination. If the activity is low, then Te^{132} is best measured by β-γ coincidence counting, using the 668 keV γ-ray of I^{132}. Beta self-adsorption corrections must be applied, however.

Average yield: 83±5%.

3. Purification of Se

1) Transfer the 31 ml Se fraction (3 *M* HCl) from the Se-Te column to a 150 ml beaker. Add 1 mg $FeCl_3$ carrier and 45 ml HCl saturated with SO_2.

2) Allow to stand 20 min. Bubble SO_2 through the solution if necessary to coagulate precipitate.

3) Filter onto a glass fiber disk. Wash with 8 *M* HCl containing SO_2 and a little $FeCl_3$ carrier, then with water and acetone.

4) Mount between scotch tape and count the 136 keV γ-ray of 120-day Se^{75} on a NaI crystal.

Average yield: 72±4%.

Thallium

1) Pass the Tl fraction from Column A (115 ml 0.1 *M* H_2SO_3) through a cation exchange column [plastic, 5.1 x 0.79 cm (v = 2.5 ml), AG50W-X8, 200-400 mesh, conditioned with H_2O and 0.1 *M* H_2SO_3]. Elute as shown in the table below.

The load solution will be a mixture of H_2SO_3 and H_2SO_4, owing to air oxidation, and so D_v's for 0.1 M H_2SO_4 should be applicable as lower limits. Tl^+ (D_v = 236) and other cations will stick, whereas anions will pass through.

Volume		Reagent	Species Eluted	Disposition	Notes
ml	v				
94	38	Load (0.1 *M* H_2SO_3)	Ir, other anions	Discard	
5	2	H_2O	H_2SO_3	Discard	a
20	8	5 *M* HF	Pa, Fe	Discard	b
20	8	0.1 *M* $HClO_4$	HCl, HF	Discard	a
20	8	4 *M* $HClO_4$	Tl, cations	Step 2	c

(a) Thoroughly rinse reservoir before adding eluent.

(b) Distribution coefficients in this medium are not well known, but should be of the following order: $Tl^+ \approx 1700$, Pa small, Fe^{2+} and $Fe^{3+} < 1$.

(c) $V_{50} \approx 2.7v$, $V_{99} \approx 5$ v (Rangnekar and Khopkar, 1966). Also, D_v in 4 M HNO_3 (which should be similar to 4 M $HClO_4$): $Tl^+ = 3.3$, most cations 2-10 (Strelow et al., 1965). It is feasible to separate certain other cations (Cu, Cd, Zn, Mn, Co, Ni, U, V, and Ag) by elution with 1 M H_2SO_4, and others (Zr, Ce, Ba, Th, Bi, Fe, Sb) by complexing with EDTA, citric, or tartaric acid (Rangnekar and Khopkar, 1966). If desired, 4 M H_2SO_4 or HNO_3 can be used as eluents.

2) Check the γ-ray spectrum of the Tl-fraction from the column, and add 1 mg each of the appropriate holdbacks. Heat to near boiling, add 1 ml H_2SO_3 to reduce any Tl^{3+} to Tl^{3+}, dropwise add 2 ml 1 *M* NaI (not KI - otherwise $KClO_4$ will precipitate), and let the solution stand for 30 min, until the yellow or orange TlI precipitate has settled.

The solubility product of TlI is 8.9×10^{-8}, so the equilibrium solubility of Tl^+ should be 0.25 mg/l in 0.07 M I^-, but 61 mg/l in water.

3) Filter the precipitate onto a paper disk, wash with 0.05 *M* NaI until neutral, then with 50% ethanol, followed by methanol. Dry at 110°C.

4) Check radiochemical purity on a γ-spectrometer: no γ's above 0.1 MeV should be present. Count the Tl^{204} β^- activity on a low-background β-proportional counter. Correct the activity for self-absorption (Fig. 12). If the activity is sufficiently high, the

Hg-K-x-ray following electron capture (2.1% abundance) may be counted. As a further check on purity, count the sample several months later, to confirm absence of short-lived contaminants.

Average yield: 63±4%.

Tin

A. LiOH-LiCl Medium

When Sn is eluted from Column B with 0.5 M LiOH-0.5 M LiCl (Fig. 9; see also Hamaguchi et al., 1969), it is clean enough for direct counting on a Ge(Li) detector. The chemical yield is determined by reirradiation. If W is present, see "Separation of Tin and Tungsten".

B. HCl-HF Medium

In some runs, Sn was stripped from Column B with 12 v 2 M HCl-3 M HF (Fig. 10). The principal contaminants, Hf and Mo, were removed by an anion exchange separation, as outlined below. Sn was eluted with LiOH-LiCl, and counted in liquid form. It can also be recovered in solid form (as SnO_2 *via* SnS_2*) but the procedure is rather time-consuming.*

1) To the Sn fraction (60 ml 2 *M* HCl-3 *M* HF), add 60 ml HCl, to make [HCl] = 7 *M*. Pass the solution through a plastic anion exchange column, AG1-X10, 200-400 mesh, 5.1 x 0.8 cm (v = 2.5 ml), conditioned with 7 *M* HCl. D_v's are:

	Sn	Mo	W	Hf
7 *M* HCl - 1.5 *M* HF	~1500	32	2.2	<1
1 *M* HCl	1000	4.5	hydrol.	hydrol.
0.5 *M* NaOH - 0.5 *M* NaCl	<<6			

Volume		Reagent	Species Eluted	Disposition
ml	v			
120	48	Load (7 *M* HCl - 1.5 *M* HF)	W, Hf	Discard
20	8	7 *M* HCl - 1.5 *M* HF	(W, Hf)	Discard
40	16	1 *M* HCl	Mo, F^-	Discard
5	2	H_2O	HCl	Discard
5	2*	0.5 *M* LiOH - 0.5 *M* LiCl	Sn	Step 2; Fig. 9

**About 77-84% of the Sn appears in the first 2 v, but the remainder elutes slowly and incompletely (Fig. 9).*

2) Count the Sn in a 1 dram glass vial. If a precipitate appears, add 1-2 drops HCl. Take an aliquot by weight for chemical yield determination by re-irradiation.

Separation of Tin and Tungsten

Tungsten behaved very erratically on Column B, often sticking to the resin instead of appearing in the initial, 4 M HCl effluent (Rb,Cs-W fraction). It then eluted with the Sn fraction (LiOH-LiCl), requiring a subsequent Sn-W separation.

1) Adjust the LiOH-LiCl fraction to $[Cl^-] \leq 0.6$ *M* and [HF] = 1 *M*. If the solution has been acidified with HCl, it will have to be evaporated to dryness, taken up in a minimum of 0.1 *M* HCl (H_2O would be better, but may cause hydrolysis) and then transferred to a polypropylene beaker before adding HF. The HF should dissolve any insoluble hydrous oxides of W or Sn. Heat if necessary.

In mixtures of 1 M HF-HCl, D_v's Sn and W fall rapidly with increasing [HCl]. For reasonably good adsorption from the necessarily large volume (~30 ml, or ~7V), it is essential to keep $[Cl^-]$ below 1 M (D_v Sn = 31, W = 33) or preferably 0.5 M (D_v Sn = 190, W = 60).

2) Load the solution on a plastic anion exchange column (AG1-X10, 200-400 mesh, 8.8 x 0.79 cm, v = 4.3 ml), conditioned with 0.5 *M* HCl-1 *M* HF. Elute as follows.

Volume ml	v	Reagent	Species Eluted	Disposition	Notes
30	7	Load (0.6 *M* Cl^--1 *M* HF)	Li	Discard	
17	4	Wash (0.5 *M* HCl-1 *M* HF)	(Li)	Discard	
26	6	5 *M* HCl - 2 *M* HF	W	W purification	a
13	3	H_2O	HCl, HF	Discard	
22	5	0.5 *M* LiOH - 0.5 *M* LiCl	Sn	Sn purification	

(a) D_v of W in this medium is not accurately known, but probably lies between 2.4 and 7.

3) Count the W fraction or purify as needed.

4) To the Sn fraction, add 1 mg 13% TAA and cautiously add 6 *M* H_2SO_4 until the solution is slightly acidic, causing yellow SnS_2 to precipitate. (Final acidity should be well below 1 *M*, because SnS_2 is appreciably soluble in acid solutions of high Cl^- concentration). Filter through filter paper and wash 2-3x with 0.1 *M* NH_4NO_3 containing some TAA, followed by a brief wash with H_2O (precipitate may peptize), and acetone. Determine the chemical yield by reirradiation.

If desired, the SnS_2 precipitate can be converted to SnO_2. Boil the precipitate with $HClO_4$ - HNO_3, dilute with H_2O, filter, mount, and count.

Zinc

1) To the 42 ml Zn fraction, add 1 mg each of Fe^{3+}, Co^{2+}, Cd^{2+}, La^{3+}, Cr^{3+}, and Sc^{3+} holdback carriers. Add 3 ml 6 *M* HCl (to make [HCl] = 0.5 *M*). If much Fe^{59} is present, add 5 ml saturated H_2SO_3.

2) Recondition the anion exchange column previously used for Cd (1 x 5 cm, AG 1-X10 resin, 200-400 mesh, Cl^- form; nominal v = 3.9 cm^3), by passing 30 ml of 0.5 *M* HCl through it.

3) Load the solution from step 1 onto the column. Adjust the flow rate to no more than 2.5 cm/min (even 1 cm/min if you have the time). Elute as follows.

Volume		Reagent	Species Eluted	Disposition	Notes
ml	v				
50	13	Load (0.5 *M* $HCl+H_2SO_3$)	Fe,Cr,Sc,Co	Discard	
27	7	Wash (0.5 *M* $HCl+H_2SO_3$)		Discard	
16	4	Wash (0.5 *M* HCl)	H_2SO_3	Discard	Rinse reservoir
23	6	0.03 *M* HCl	Zn	Step 4	Rinse reservoir

4) Check γ-ray spectrum of Zn fraction. If clean, proceed to step 7, otherwise add appropriate holdbacks and purify according to steps 5 and 6. (If Fe^{59} is the only contaminant, add 10 mg Fe^{3+} carrier and 1 ml saturated H_2SO_3, to reduce Fe^{3+} to Fe^{2+}, and proceed to step 7).

5) Add 5 mg of Fe^{3+} carrier and make basic with 6 *M* NH_4OH. Heat, centrifuge, and discard the $Fe(OH)_3$ precipitate.

6) Neutralize the supernate (transient appearance of $Zn(OH)_2$ indicates the neutral point) and make 1 *M* in HCl.

7) Add 10 ml of saturated oxalic acid and $K_2Hg(SCN)_4$ reagent (39 g KCNS + 27 g $HgCl_2$ in 1000 ml H_2O), in a ratio of 1 ml reagent for each 4 ml of sample solution, and allow the mixture to stand for 1 hour to precipitate $ZnHg(SCN)_4$. Stir again after 5 minutes. In pure water, $ZnHg(SCN)_4$ has a solubility of 3.7×10^{-4} M/l, or 24 mg Zn^{2+} per liter.

8) Filter the precipitate onto a glass fiber disk. Wash with diluted reagent (1:100), then briefly with H_2O and acetone. Dry at 110°C, and mount between scotch tape (gravimetric factor 0.1312). Count on a NaI crystal.

Average yield: 85±7%.

E. APPENDIX

1. Shorter Procedure for Crater Samples

(Au, Cs, Ge, Ir, Ni, Os, Pd, Rb, Se)

After the Os-distillation, the conversion to chlorides and the separation of Ag are done as usual. The load solution for Column A can be made 0.5 *M* in HCl if no F^- is added to complex Pa (in which case Fe elutes with Ni), but it must be made 3 *M* if F^- is added. Data below are for a 10 cm column (v = 7.85 ml), which is long enough in view of the smaller loading.

Volume ml	Volume v	Reagent	Species Eluted	Disposition	Notes
≤12	≤1.5	Load (3 *M* $HCl+Ce^{4+}+HF$)	} Ni,Co,REE,Mg, Pa Cr, Mn	} Ni pur.	
12	1.5	Wash (3 *M* HCl+HF)			
110	14	0.001 *M* HCl	*F^-,Fe,In,Te,Zn,Cd*		
94	12	0.1 *M* H_2SO_3	Tl	Discard	
94	12	6 *M* HCl	Ir	Ir pur.	b
15	2	Aqua regia-H_2O (1:1)	-	Discard	
23	3	H_2O	*(Ir)*	Discard	
47	6	1 *M* $HClO_4$-0.003 *M* HCl	Pd *(Bi)*	Pd pur.	
8	1	H_2O	*$HClO_4$*	Discard	
79	10	10% thiourea	Au	Au pur.	

(a) Thoroughly rinse reservoir before adding eluent.
(b) If no Tl carrier is present, then less than 12 v H_2SO_3 may be used.

The remaining elements (Ge, Se, Rb, Cs) are recovered by the usual procedure, except that Column B is omitted (unless Re is to be measured). Rb and Cs are then sought in the supernate from the Se, Te precipitation.

2. Treatment of the Standards

Opening, dissolution and equilibration

Dissolve In		Digest Overnight	Convert To
a. Ag-Se-Pd	conc. HNO_3+1 drop H_2O_2	hot plate*	0.5 *M* HNO_3 (100 ml)
b. Ni-In-Zn-Cd-Au	aqua regia	hot plate	conc. HCl (100 ml)
c. Te-Tl-Bi	conc. HNO_3	hot plate	7.5 *M* HNO_3 (100 ml)
d. Br-Cs-Rb	NaOH - see procedure		
e. Ge-Sb-Sn-Re	3 *M* HCl	room temp.	3 *M* HCl (100 ml): let equilibrate for 1-2 days
f. Ir	conc. HCl	hot plate	conc. HCl (100-250 ml)
g. Os-W	2 *M* HCl(SO_2) before opening the silica tube is cooled in liquid nitrogen	refrigerator	2 *M* HCl

**This standard must be processed quickly, because silver precipitates if exposed to light or HCl fumes.*

After making up to volume, pipet the appropriate quantities for the standards, together with the carriers. Process as described in the following pages. All standards are prepared in duplicate.

3. Procedure for Individual Standards

a. Ag-Se-Pd standard

1) To 3 ml of the 0.5 *M* HNO_3 solution, add 3 ml each of Ag, Se, and Pd carriers. Heat briefly to ensure exchange, cool, and precipitate AgCl with 1 ml 1 *M* HCl. (Don't use stronger acid - AgCl is somewhat soluble at higher [HCl]). Save the solution for step 5.

2) Wash the AgCl precipitate 3 times with 0.5 *M* HNO_3, and dissolve it in 10 ml 6 *M* NH_4OH. Add 1 mg Se holdback and 5 mg Fe^{3+} carrier, stir, centrifuge, and discard the $Fe(OH)_3$ precipitate. Check the γ-spectrum of the solution on a Ge(Li) detector for Se contamination. If present, proceed to Step 3, otherwise to Step 4.

3) Add 1 ml 1 *M* HCl to the supernate and acidify with 6 *M* HNO_3 to precipitate AgCl. Centrifuge, wash 3 times with 0.5 *M* HNO_3, and dissolve in 10 ml 6 *M* NH_4OH. Add 1 mg Se holdback and 1 ml 1 *M* HCl.

4) Acidify with 6 *M* HNO_3. Filter immediately onto a fiberglass disk, before the AgCl precipitate has coagulated. Wash with water and acetone. Dry at 110°C.

5) Add a few ml of conc. HCl to the Se-Pd solution from step 1 and evaporate to dryness, to convert nitrates to chlorides. Repeat. Take up in 8 ml 4 *M* HCl and load the solution on an anion exchange column [AG1-X10, 200-400 mesh, Cl^- form; 1x10 cm (v = 7.9 ml)]. Elute as follows:

Volume ml	Volume v	Reagent	Species Eluted	Disposition	Notes
8	1	Load (4 *M* HCl)	Se	} Step 6	
8	1	Wash (4 *M* HCl)	Se		
40	5	8 *M* HCl	(Ag, Se)	Discard	a
8	1	H_2O	HCl	Discard	
47	6	1 *M* $HClO_4$-0.003 *M* HCl	Pd	Step 7	

(a) Thoroughly rinse reservoir before adding eluent.

6) To the Se fraction (16 ml), add an equal volume of HCl, to make [HCl] = 8 *M*. Heat to about 60° and precipitate Se with 1 ml hydrazine hydrochloride solution. Wash with 8 *M* HCl, then with water, and finally with acetone.

There is some reason to worry about isotopic exchange of active and carrier Se, because some of the initial Se(VI) in the standard may have transformed to Se(IV) by hot-atom reactions. In the present procedure, a drop of H_2O_2 *is added to the initial conc.* HNO_3 *solution, to oxidize any Se(IV) to Se(VI). Hydrazine rather than* SO_2 *is used to precipitate Se because* SO_2 *reacts very slowly with Se(VI). Another possibility is to evaporate a 12 M HCl solution to near dryness, which reduces Se(VI) to Se(IV), and then to precipitate Se with* SO_2*.*

7) Warm the Pd fraction to about 80°C on a water bath. Dropwise add dimethyl glyoxime (1% in ethanol) until no more precipitate forms (about 4-5 ml should be required). Cool to room temperature.

It should be feasible to precipitate Pd directly from the supernate in step 1, after adding a few mg Ag^+ *carrier to remove the remaining traces of active* Ag^+ *as AgCl. After precipitating Pd with dimethyl glyoxime, the supernate is twice evaporated to dryness with HCl, and Se is precipitated with hydrazine hydrochloride as in step 6. Any traces of Pd remaining would probably be reduced also, but both the amount and the radiation level should be negligible.*

b. Ni-In-Zn-Cd-Au standard

1) Evaporate to near dryness, and dissolve in 10 ml 3 *M* HCl.

2) Prepare two anion exchange columns [AG1-X10, 200-400 mesh; 1x10 cm (v = 7.9 ml)]. Condition with 30 ml 3 *M* HCl.

3) Load solution onto the columns. Elute according to the following table:

Volume ml	Volume v	Reagent	Species Eluted	Disposition	Notes
10	1.3	Load (3 *M* HCl)	Ni, other cations	Step 4	
8	1	Wash (3 *M* HCl)			a
16	2	3 *M* HCl	Ni, etc.	Discard	
95	12	3 *M* HCl	In	Step 5	a
63	8	0.5 *M* HCl	In,Te,Fe	Discard	
63	8	0.03 *M* HCl	Zn	Step 6	
95	12	0.002 *M* HCl	Cd	Step 7	a
47	6	10% Thiourea	Au	Step 8	

(a) Thoroughly rinse reservoir before adding eluent.

4) To the Ni fraction, add 1 mg each of Fe^{3+}, Co, La, Mn, and Sc carriers, and 1 drop H_2O_2 (3%). Neutralize with 6 *M* NH_4OH (about 9 ml) until a $Fe(OH)_3$-MnO_2 precipitate forms, then add 2 ml in excess so that $[NH_3] \approx 0.2$ *M* and the pH is between 8 and 9. Centrifuge and discard the precipitate. Precipitate $Ni(DMG)_2$ according to steps 3 and 4 of the sample procedure.

5) The In fraction should be clean enough for precipitation according to steps 3-5 of the sample procedure; if not, it can first be purified by steps 1-2.

6) Precipitate Zn as $Zn[Hg(SCN)_4]$, according to steps 6-8 of the sample procedure. The sample usually is radiochemically clean.

7) Precipitate Cd as $CdNH_4PO_4$ according to steps 5-7 of the sample procedure. The sample is radiochemically clean.

8) Precipitate Au_2S_3 and purify according to the sample procedure.

(A long-lived, interfering nuclide tends to get through here. Either use a Ge-Li detector, or repeat the hydroquinone precipitation).

c. Te-Tl-Bi standard

1) Take ~1/10 of the standard solution, evaporate to dryness, take up the residue in 10 ml HCl, add 1 mg Ir carrier and 2 ml 5 *M* LiCl, and evaporate again. Dissolve the residue in 12 ml 3 *M* HCl by warming for a few minutes. Cool and add 1 ml 0.2 *M* $Ce(SO_4)_2$ in 1 *M* H_2SO_4, to ensure that all Ir is oxidized from +3 to +4.

2) Load the supernate onto an anion exchange column [AG1-X10, 200-400 mesh, Cl^- form, 1x12 cm (v = 9.4 ml)], conditioned shortly before use with 15 ml 0.5 *M* HCl + 0.05 *M* Ce(IV) (freshly mixed from a stock solution of 0.2 *M* $Ce(SO_4)_2$ in 1 *M* H_2SO_4), then with 30 ml 3 *M* HCl. Wash with 9 ml 3 *M* HCl and elute as follows.

Volume		Reagent	Species Eluted	Disposition	Notes
ml	v				
12	1.3	Load (3 *M* $HCl+Ce^{4+}$)	} Cations (Ir)	Discard	a
9	1	Wash (3 *M* HCl)			
19	2	3 *M* HCl	(Ir?)	Discard	a
38	4	0.5 *M* HCl	Te,(Fe)	Step 3	
113	12	0.002 *M* HCl	Cd,Zn	Discard	
94	10	1 *M* H_2SO_4	Bi	Step 4	a
57	6	0.1 *M* H_2SO_3-0.1 *M* H_2SO_4	Tl	Tl pur.	

(a) Thoroughly rinse reservoir before adding eluent, to prevent contamination with previous solution.

3) Precipitate Te according to steps 5-6 of the Te procedure.

4) Purify the Bi fraction according to the sample procedure. The Bi fraction can be loaded directly on the anion exchange column, by making it 1 *M* in HCl.

d. Br-Cs-Rb standard

The steps required only for Br are given in italics, and can be omitted if Br is not measured. Note that Br alone is largely recovered by steps 4-7, but that Rb and Cs require an NaOH etch, as described in step 8.

1) Wash the silica tube in aqua regia and with water.

2) Cool the tube in liquid N_2.

3) Cut the tube *and transfer into Br carrier beaker.*

4) Add several drops of 6 M NaOH and 1 ml of NaOCl. Let stand for 1 hr.

5) Carefully add 1 ml of 1 M Na_2SO_3 and dilute H_2SO_4 to neutralize the solution. Let stand for at least 1 hr.

6) Quantitatively transfer the solution to a 250 ml volumetric flask.

7) Wash the silica tube with a few drops of 1 M Na_2SO_3 and ~2 M H_2SO_4. Repeat several times.

8) Set silica tube upright in the carrier beaker. Add several drops of Rb-Cs carrier solution (without Cs^{137} tracer) and 6 *M* NaOH to etch the inside surface of the silica tube. Let stand for at least 1 hr.

9) Transfer the solution to a 250 ml volumetric flask. Wash the silica tube with dilute H_2SO_4 several times. Transfer the washings into the 250 ml volumetric flask and make up to volume with dil. H_2SO_4, so that the final acidity is ~4 *N* in H_2SO_4.

10) Take 2 ml of this solution as the Rb-Cs standard.

11) Extract Br_2 from an aliquot of the solution by the same procedure as used for the samples, but with only 1 ml saturated $KMnO_4$ solution.

e. Ge-Sb-Sn-Re Standard

1) Prepare two plastic anion exchange columns, AG1-X10, 200-400 mesh, Cl^- form, 8.8 x 0.79 cm (v = 4.3 ml), with dacron fiber plugs. Condition the columns with 20 ml 3 *M* HCl.

2) To the sample solution (≤20 ml 3 *M* HCl) add 1 mg Fe^{3+} carrier and 1 ml sat. H_2SO_4 or 3 *M* $NH_2OH \cdot HCl$, to reduce Fe^{3+} to Fe^{2+} and Sb(V) to Sb(III). Load the solution onto the column, and elute according to the following table.

Volume ml	Volume v	Reagent	Species Eluted	Disposition	Notes
≤22	≤5	Load (3 *M* HCl)	Ge,cations,As, Fe	Step 3	
22	5	Wash (3 *M* HCl)			
26	6	0.3 *M* HCl-1 *M* HF	Sb	Step 4	a
17	4	1 *M* HCl	HF	Discard	a
26	6	0.5 *M* LiOH-0.5 *M* LiCl	Sn	Step 5	
26	6	0.2 *M* $HClO_4$	Cl^-,Ir	Discard	
13	3	2 *M* $HClO_4$	ReO_4^-	Step 6	

(a) Rinse reservoir before adding eluent.

3) Adjust acidity of Ge fraction to 8-9 *M* HCl, extract Ge into CCl_4, and precipitate as GeS_2, according to procedure C2.

4) Precipitate metallic Sb, according to step 5 of the sample purification procedure.

5) Dilute Sn fraction to appropriate volume and take aliquot for counting on Ge(Li) detector.

6) Precipitate Re first as Re_2S_7 and then as Φ_4AsReO_4, according to steps 5-8 of the sample procedure.

f. Ir Standard

Pipet the appropriate amount into a counting vial.

g. Os-W Standard

1) Pipet 3 ml standard solution + 3 ml Os and W carrier solutions into a Zr crucible. Neutralize with 6 *M* NaOH and dry under a heat lamp.

2) Fuse with NaOH + Na_2O_2 for 15 min. Cool and dissolve in water.

3) Transfer the solution to a distilling flask, and treat according to the Os purification procedure.

4) Toward the end of the OsO_4 distillation (step 3 of the Os procedure), stop adding H_2O_2 and continue heating until all the H_2O_2 has decomposed. Let the flask cool and centrifuge off the yellow WO_3.aq. precipitate. Wash twice with 20 ml 6 *M* HNO_3.

5) Dissolve the WO_3 precipitate in 1 *M* NH_3 and purify as needed.

If Os persists in the W fraction, it can be removed by an evaporation with HNO_3 *in step 4.*

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BIBLIOGRAPHY

Anders, E., Sen Sarma, R.N., and Miller, J.M., 1959, *J. Phys. Chem.*, 63, 559-565.

Anders, E. and Ebihara, M., *Geochim. Cosmochim. Acta*, 46, 2363-2380.

Anders, E., Higuchi, H., Ganapathy, R., and Morgan, J.W., 1976, *Geochim. Cosmochim. Acta* 40, 1131-1139.

Atkins, D.H.F. and Smales, A.A., 1960, *Anal. Chim. Acta*, 22, 462-478.

Beamish, F.E. and Dale, J., 1938, *Ind. Eng. Chem.* (Anal. Ed.) 10, 697-8.

Beamish, F.E., Russell, J.J., and Seath, J., 1937, *Ind. Eng. Chem.* (Anal. Ed.) 9, 174-176.

Binz, C.M., Kurimoto, R.K., and Lipschutz, M.E., 1974, *Geochim. Cosmochim. Acta* 38, 1579-1606.

Burgus, W.H., 1954, *U.S.A.E.C. Report No. LA-1721*, U.S.A.E.C., Washington, D.C., Ni 1.

Chung, K.S. and Beamish, F.E., 1968a, *Talanta* 15, 823-829.

Chung, K.S. and Beamish, F.E., 1968b, *Analyt. Chim. Acta*, 43, 357-368.

Crocket, J., Keays, R.R., and Hsieh, S., 1968, *J. Radioanal. Chem.*, 1, 487-507.

Ebihara, M., 1985, *Anal. Sci.*, 1, 241-246.

Ebihara, M., Wolf, R., and Anders, E., 1982, *Geochim. Cosmochim. Acta* 46, 1849-1861.

Fresenius, C.R. and Jander, G., *Handbuch der analyt. Chemie* (Ge Volume, p. 8).

Fritz, J.S. and Rettig, T.A., 1962, *Anal. Chem.*, 34, 1562-1566.

Geilmann, W. and Gebauhr, W., 1953, *Z. Anal. Chem.*, 139, 161-181.

Glendenin, L.E., 1951, *Radiochemical Studies: The Fission Products*, Book 3, Part VI, McGraw-Hill, New York.

Gros, L., Takahashi, H., Hertogen, J., Morgan, J.W., and Anders, E., 1976, *Proc. Lunar Sci. Conf. 7th*, 2403-2425.

Grossman, L. and Larimer, J.W., 1974, *Rev. Geophys. Space Phys.*, 12, 71-107.

Hamaguchi, H., Onuma, N., Hirao, Y., Yokoyama, H., Bando, S., and Furukawa, M., 1969, *Geochim. Cosmochim. Acta*, 33, 507-518.

Hertogen, J., Janssens, M.-J., Takahashi, H., Palme, H., and Anders, E., 1977, *Proc. Lunar Sci. Conf. 8th*, 17-45.

Hertogen, J., Janssens, M.-J., and Palme, H., 1980, *Geochim. Cosmochim. Acta* 44, 2125-2143.

Hertogen, J., Janssens, M.-J., Takahashi, H., Morgan, J.W., and Anders, E., 1983, *Geochim. Cosmochim. Acta* 47, 2241-2255.

Higuchi, H., Morgan, J.W., Ganapathy, R., and Anders, E., 1976, *Geochim. Cosmochim. Acta* 40, 1563-1571.

Janssens, M.-J., Hertogen, J., Wolf, R., Ebihara, M., and Anders, E., 1987, *Geochim. Cosmochim. Acta*, 51, 2275-2283.

Keays, R.R., Ganapathy, R., Laul, J.C., U. Krähenbühl, and Morgan, J.W., 1974., *Analyt. Chim. Acta* 72, 1-29.

Kimura, K., Lewis, R.S., and Anders, E., *Geochim. Cosmochim. Acta*, 38, 683-701.

Knowles, H.B., 1932, *J. Res. Natl. Bur. Stds.*, 9, 1-7.

Kolthoff, I.M. and Elving, P.J., eds. 1963, *Treatise on Analytical Chemistry*, Part II, Vol. 8.

Kraus, K.A. and Nelson, F., 1956, *Proc. First Intern. Conf. Peaceful Uses At. Energy*, Geneva, 1955, Vol. VII, United Nations, New York, 113.

Krähenbühl, U., Morgan, J.W., Ganapathy, R., Anders, E., 1973, *Geochim. Cosmochim. Acta*, 37, 1353-1370.

Laul, J.C., 1969, Ph.D. dissertation, Purdue University.

Laul, J.C., 1977, *Neutron Activation Analysis in Geological Materials*, BNWL-SA-6280, UC-2, Batelle Report, 70.

Laul, J.C., 1979, *At. Energy Rev.*, 17, 603-695.

Laul, J.C., Case, D.R., Schmidt-Bleek, F., and Lipschutz, M.E., 1970a, *Geochim. Cosmochim. Acta*, 34, 89.

Laul, J.C., Pelly, I., and Lipschutz, M.E., 1970b, *Geochim. Cosmochim. Acta*, 34, 909.

Leddicotte, G.W., 1961, *The Radiochemistry of Osmium*, NAS-NS 3046, U.S.A.E.C., Washington, D.C.

Leddicotte, G.W., 1961, *The Radiochemistry of Tellurium*, NAS-NS 3038, U.S.A.E.C., Washington, D.C.

Marinsky, J.A., 1961, *The Radiochemistry of Germanium*, NAS-NS 3043, U.S.A.E.C., Washington, D.C.

Miller, E.H. and Page, W., 1901, *Z. Anorg. Chem.*, 28, 233.

Molinski, V.J. and Leddicotte, G.W., 1965, *The Radiochemistry of Selenium*, NAS-NS 3030 (Rev.), U.S.A.E.C., Washington, D.C.

Morgan, J.W., 1965, *Anal. Chim. Acta*, 32, 8-16.

Morgan, J.W., 1977, *J. Radioanalyt. Chem.*, 37, 79-118.

Morgan, J.W., 1978, *Proc. Lunar Planet. Sci. Conf. 9th*, 2713-2730.

Morgan, J.W. and Wandless, G.A. 1979, *Lunar Planet. Sci. X*, 855-857.

Morgan, J.W. and Wandless, G. A. 1983, *Proc. Lunar Planet. Sci. Conf. 13th, J. Geophys. Res.*, 88, A819-A829.

Morgan, J.W., Higuchi, H., Ganapathy, R., and Anders, E. 1975, *Proc. Lunar Sci. Conf. 6th*, 1609-1625.

Morgan, J.W., Ganapathy, R., Higuchi, H., and Krähenbühl, U., 1976, *Geochim. Cosmochim. Acta* 40, 861-887.

Morgan, J.W., Ganapathy, R., Higuchi, H., and Anders, E., 1977, The Soviet-American Conference on Cosmochemistry of the Moon and Planets (J.H. Pomeroy and N.J. Hubbard, eds.) *NASA SP-370*, 659-689.

Morgan, J.W., Higuchi, H., Takahashi, H., and Hertogen, J., 1978, *Geochim. Cosmochim. Acta* 42, 27-38.

Morgan, J.W., Janssens, M.-J., Hertogen, J., Gros, J., and Takahashi, H., 1979, *Geochim. Cosmochim. Acta* 43, 803-815.

Morgan, J.W., Wandless, G.A., Petrie, R.K., and Irving, A.J., 1980, *Proc. Lunar Planet. Sci. Conf. 11th*, 213-233.

Morgan, J.W., Wandless, G.A., Petrie, R.K., and Irving, A.J., 1981, *Tectonophys*, 75, 47-67.

Morgan, J.W., Janssens, M.-J., Takahashi, H., Hertogen, J., and Anders, E., 1985, *Geochim. Cosmochim. Acta* 49, 247-259.

Nelson, F. and Kraus, K.A., 1960, *J. Chromatogr.*, 3, 279-281.

Noyes, A.A. and Bray, W.C., 1927, *A System of Qualitative Analysis for the Rare Elements*, Macmillan, New York.

Palme, H., Janssens, M.-J., Takahashi, H., Anders, E., and Hertogen, J., 1978, *Geochim. Cosmochim. Acta* 42, 313-323.

Palme, H., Göbel, E., and Grieve, R.A.F., 1979, *Proc. Lunar Planet. Sci. Conf., 10th, Geochim. Cosmochim. Acta*, 2465-2492.

Palme, H., Grieve, R.A.F., and Wolf, R., 1981, *Geochim. Cosmochim. Acta* 45, 2417-2424.

Prestwood, R.J., in Marinsky (1961).

Rangnekar, A.V. and Khopkar, S.M., 1966, *Indian J. Chem.*, 4, 318-320.

Rayner, H.B., 1963, *Analyt. Chem.*, 35, 1097-1098.

Schindewolf, U., 1960, *Geochim. Cosmochim. Acta*, 19, 134-138.

Smales, A.A., van R. Smit, J., and Irving, H., 1957, *Analyst*, 82, 539-549.

Steinnes, E., 1971, *Activation Analysis in Geochemistry and Cosmochemistry*, (A.O. Brunfelt and E. Steinnes, eds.) Universitetsforlaget, Oslo, 113-128.

Strelow, F.W.E. and Bothma, C.J.C., 1967, *Anal. Chem.*, 39, 595-599.

Strelow, F.W.E., Rethemeyer, R., and Bothma, C.J.C., 1965, *Anal. Chem.*, 37, 106-111.

Takahashi, H., Janssens, M-J., Morgan, J.W., and Anders, E., 1978, *Geochim. Cosmochim Acta* 42, 92-106.

Tanner, J.T. and Ehmann, W.D., 1967, *Geochim. Cosmochim. Acta*, 31, 2007.

Tomura, K., Higuchi, H., Takahashi, H., Onuma, N., and Hamaguchi, H., 1968, *Anal. Chim. Acta*, 43, 523.

Walsh, T.J. and Hausman, E.A., 1963, "The Platinum Metals" in: *Treatise on Analytical Chemistry*, I.M. Kolthoff and P.J. Elving, eds.

Wandless, G.A., and Morgan, J.W., 1985, *J. Radioanalyt. Nucl. Chem.*, 92, 273-282.

Wasson, J.T., 1985, *Meteorites: Their Record of the Early Solar System*, Appendix G, p. 250-252, Freeman and Co., New York, 267 pages.

Westland, A.D. and Beamish, F.E., 1954, *Anal. Chem.*, 26, 739-741.

Westland, A.D. and Beamish, F.E., 1957, *Microchim. Acta*, 625-639.

Wilson, C.L. and Wilson, D.W., eds. 1962, *Comprehensive Analytical Chemistry*. Classical Analysis: Gravimetric and Titrimetric Determination of the Elements, Vol. IC, Elsevier Publishing Co., Princeton.

Wolf, R. and Anders, E., 1980, *Geochim. Cosmochim. Acta* 44, 2111-2124.

Wolf, R., Woodrow, A.B., and Grieve, R.A.F., 1980, *Geochim. Cosmochim. Acta* 44, 1015-1022.

Wolf, R., Richter, G.R., Woodrow, A.B., and Anders, E., 1980, *Geochim. Cosmochim. Acta*, 44, 711-717.

Wolf, R., Ebihara, M., Richter, G.R., and Anders, E., 1983, *Geochim. Cosmochim. Acta* 47, 2257-2270.

Yagoda, H. and Fales, H.A., 1938, *J. Am. Chem. Soc.*, 60, 640-643.