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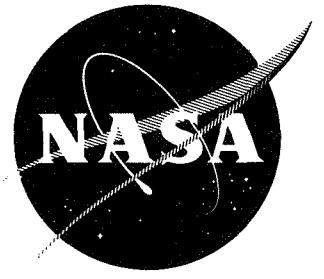

PREPARATION OF PURE LITHIUM HEXAFLUOROARSENATE

by

Edward W. Lawless

MIDWEST RESEARCH INSTITUTE

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
Cleveland, Ohio
Patricia M. O'Donnell, Project Manager

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FINAL REPORT

PREPARATION OF PURE LITHIUM HEXAFLUOROARSENATE

by

Edward W. Lawless

MIDWEST RESEARCH INSTITUTE
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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

May 20, 1970

CONTRACT NAS 3-12979

NASA Lewis Research Center
Cleveland, Ohio
Patricia M. O'Donnell, Project Manager

FOREWORD

This Final Report describes the research performed at Midwest Research Institute during the period 15 June 1969 to April 15 1970 on Contract NAS 3-12979. Mrs. Patricia M. O'Donnell has been Project Manager for the Lewis Research Center of the National Aeronautics and Space Administration.

This program (MRI Project No. 3325-C) has been under the general supervision of Dr. A. D. McElroy, Head, Inorganic Chemistry Section of MRI's Physical Sciences Division. Dr. E. W. Lawless, Project Leader, was assisted in carrying out the program by Mr. Yukio Mizumoto, Mr. C. J. Wesley Wiegand and Mrs. Constance Weis. Dr. Evelyn Murrill, Mrs. Hope Miller and Mr. George Vaughn performed special instrumental analyses.

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ABSTRACT

Methods for the preparation and analysis of high purity lithium hexafluoroarsenate, $LiAsF_6$, were studied. Two thousand grams of $LiAsF_6$ were ultimately prepared by neutralization of aqueous $HAsF_6$ with LiOH solution followed by multiple recrystallization of $LiAsF_6 \cdot 3H_2O$ from water and vacuum drying at 40°C to yield the anhydrous salt. The final product contained not more than 100 ppm of any impurity on an elemental basis. Two other methods for the preparation of $LiAsF_6$ were also successful, but were less suited to scale-up on the basis of product purity and experimental considerations. A fourth proposed synthesis method was unsuccessful. Analytical techniques which were used to determine product purity were carefully evaluated by exhaustive analyses of standard samples and the final product.

SUMMARY

The objective of this program was to prepare 2,000 g. of high purity lithium hexafluoroarsenate, $LiAsF_6$, which is needed for high energy density battery studies of interest to NASA. The goal was to prepare a product which contained not more than 100 ppm of any impurity on an elemental basis.

The analytical methods to be used were evaluated by multiple analyses of standard samples of LiF and As_2O_3. Analysis of the final product was made by a selected combination of methods.

Four reaction routes were selected for study based on the literature, availability and purity of starting materials, and anticipated experimental difficulties in obtaining a high purity product of $LiAsF_6$. These methods were as follows:

1. Neutralization of aqueous $HAsF_6$ with LiOH,
2. Ion exchange with $KAsF_6$,
3. Reaction of AsF_5 with LiF, and
4. Reaction of As_2O_5 with LiOH (or LiF) and HF.

The $LiAsF_6$ was successfully prepared by the first three of these methods. (The key intermediate, $LiAsF_5OH$, in method four was never successfully isolated in the anhydrous form.) Analyses of the products showed, however, that high purity $LiAsF_6$ was not produced directly by any of the three methods and each would require a recrystallization procedure to yield a high purity product. Method number one was then used to produce about 4,000 g. of crude $LiAsF_6 \cdot 3H_2O$ which was fractionally recrystallized from water and then vacuum dried at 40°C to give 2,130 g. of anhydrous $LiAsF_6$ which met the specifications. This product was sealed in 20 glass ampoules under an argon atmosphere and delivered to NASA.

I. INTRODUCTION

Lithium hexafluoroarsenate was first synthesized in 1956, but it has never been available commercially. Because of its solubility and electrochemical characteristics, it is of much interest to NASA as an electrolyte in high energy density batteries which contain nonaqueous solvents. NASA therefore contracted with Midwest Research Institute to synthesize and deliver 2,000 g. of high purity $LiAsF_6$. The goal was to prepare a product having not more than 100 ppm of any impurity on an elemental basis. The technical program consisted of four tasks:

Task 1 - Demonstrate the reliability of analytical procedures for major constituent and impurity analyses.

Task 2 - Prepare small quantities (25 g.) of $LiAsF_6$ by up to four different synthesis methods and analyze for all impurities.

Task 3 - Evaluate the synthesis methods and select the best method for scale-up, based on the purity of product and experimental considerations.

Task 4 - Prepare 2,000 g. of high purity $LiAsF_6$ by the selected method, analyze for all impurities, and deliver to NASA in sealed ampoules.

This report describes the activities and results on each of these tasks.

II. EVALUATION OF ANALYTICAL METHODS

The analytical methods for major constituent elements and impurity elements were of such importance to this program that extensive testing was made in order to establish their reliability. Most of these analyses were performed by commercial analytical laboratories and an effort was made to obtain an independent check on every method.

A. Major Constituent Elements

Lithium, arsenic and fluorine analyses were performed primarily by Schwarzkopf Microanalytical Laboratories (Woodside, New York) with preliminary or confirmatory analyses performed in a few cases at Galbraith Laboratories (Knoxville, Tennessee) and at MRI. Lithium analyses were performed by atomic absorption spectrometry at both Schwarzkopf and Galbraith and by the less precise flame photometric method at MRI. Arsenic was determined by iodometric

analysis of As(V), (i.e., addition of excess iodide and titration with thiosulfate) after a preliminary combustion with oxygen (Schwarzkopf) or Na_2O_2 (MRI). Galbraith's arsenic method (which also included a combustion step) was quite satisfactory for $LiAsF_6$, but apparently required modification for simple arsenate. Schwarzkopf performs fluoride analysis by a moist air combustion of the sample followed by titration with a lanthanum reagent. At MRI, fluoride was determined by acid distillation followed by thorium nitrate titration (with the methyl thymol blue indicator). We found, however, that this method gave low results with AsF_6^- salts unless a predistillation digestion period (at 90°C for 20-30 min.) was used to complete hydrolysis and thereby prevent partial distillation of $HAsF_6$. Galbraith's initial conventional distillation on a sample of $LiAsF_6$ thus gave very low results and a redetermination using a slow distillation (not a digestion) still did not give a full fluoride analysis. In addition, analyses were performed at MRI on some $LiAsF_6$ samples for As(V) in the form of impurities such as AsO_4^{-3}, for As(III), and for free F^-. (The detection limit for As(V) impurities is limited by the blank correction which is necessary.) Duplicate analyses on two $LiAsF_6$ samples at Schwarzkopf and Galbraith are shown on pages 18 and 22.

The calculated analysis of pure $LiAsF_6$ and the uncertainty of the analytical method for each element as reported by Dr. Schwarzkopf are as follows:

	Theoretical	Uncertainty
Li	3.54%	± 0.1%*
As	38.25%	± 0.3%
F	58.21%	± 0.3%

B. Impurity Elements

In order to establish the reliability of methods for impurity analysis two independent methods were desired for essentially each of the elements and were tested with standard samples of LiF and As_2O_3, and also on some samples of $LiAsF_6$. Spark source mass spectrometry is capable of analyzing for all elements and was selected as one method. These analyses were performed by Bell and Howell Research Laboratories (Pasadena, California). The spark source results were checked by a combination of methods consisting of emission and atomic absorption spectroscopy for metals and metalloid elements, and specific tests for the nonmetals. These analyses were performed by Coors Spectrochemical Laboratories (Denver, Colorado), Chemo-Services Associates Corporation (St. Louis, Missouri), and Schwarzkopf Microanalytical Laboratories.

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* His Li analyses on high purity $LiAsF_6$ samples were, however, consistently low, i.e., 3.35 to 3.42%. The reason is unknown.

The initial analyses on the standard LiF sample showed such wide divergences between methods and analysts that further testing was required to try to resolve the conflicts. The second spark source M.S. analysis was so different from the first that four more analyses were performed to determine if this method was reliable for fluoride salts and also to determine if the standard sample was homogeneous. The LiF, a Fisher CP Grade material, was a uniform white powder. All samples were taken from the same 4-oz. bottle and supplied to the analyst in glass vials without further treatment. It showed a weight loss of 0.4% upon vacuum drying at 135°C and fluorine analysis on the dried material indicated a minimum assay of about 97% LiF. It gave 54 mg. insoluble material (possibly silica) when dissolved at the level of 1 g/liter of water. The pH of this solution was 5.75.

The results of these exhaustive analyses on the standard LiF sample are shown in Tables I and II. Several conclusions are apparent, but some discrepancies remain unresolved. Overall, the sample appears to be slightly nonhomogeneous with respect to silica, but some variations appear to arise from analytical errors. The initial spark source M.S. analysis gave anomalously high results* for 12 elements: H, C, N, Na, P, S, Cl, K, Ca, Fe and Co. The results of the last four M.S. analyses (which were performed in sets of two each on the same day) were in reasonably good agreement with each other (with two exceptions), with the results of the second analysis (although the latter gave somewhat higher levels of S, Ca and Fe), and with the "best" result by emission and atomic absorption spectroscopy. These latter methods as employed by Coors gave extremely erratic results of sodium and aluminum (the latter being essentially nil by all other methods) and an anomalous Mo analysis. The standard As_2O_3 sample was a reagent grade material and since few impurities were present, the divergence between analysts was much less than for the LiF. The results for As_2O_3 are shown in Table III.

In general, we conclude (based on these analyses and subsequent analyses of $LiAsF_6$ samples) that the spark source M.S. method is reliable, but certain precautions are required. For example, the high sensitivity of the method combined with the volatility of the alkali metals makes Li, Na, K, etc., analyses very susceptible to high results because of cross contamination during sparking and "memory" effects or residuals in the instrument. The fluoride salts appear to pose a second problem in that sparking the sample may produce fluorine atoms or molecules. These then react quite efficiently with traces of nonvolatile residuals or with the samples loaded at the same time in the instrument to yield volatile products. The result is that high levels of such impurities as C or Si may be observed. This conclusion is based on the observations that the carbon level decreased steadily on the

* Bell and Howell suggests that instrumental malfunction may have caused more intense exposures during sparking than actually recorded.

TABLE I

SPARK SOURCE MASS SPECTROMETRIC ANALYSIS OF STANDARD LITHIUM FLUORIDE SAMPLE[a]
(Fisher CP Grade, Lot No. 74579)

Analysis No.	1	2	3	4	5	6
Sample No.[b]	79-A	109-A	109-A	109-A	79-A	79-A
Element[c]						
H	690	45	120	85	85	73
B	-	-	17	17	14	9.1
C	1,200	378	580	540	300	230
N	310	14	28	18	24	25
O	11,700	11,000	12,000	6,600	6,600	5,500
Na	5,100	94	120	92	160	150
Mg	160	25	-	-	-	-
Al	4	-	6.9	5.4	2	2
Si	2,370	5,380	1,900	3,200	1,600	1,500
P	480	-	-	-	-	-
S	1,850	217	70	130	66	70
Cl	300	65	60	38	36	14
K	930	90	22	5.4	70	17
Ca	1,100	308	55	160	43	74
Fe	1,400	112	36	56	20	43
Co	1,540	-	15	77	9.1	64
Ni	220	-	-	-	-	-
Cu	15	-	25	25	< 20	< 20
Zn	-	106	120	85	< 70	< 70

a/ Analysis by Bell and Howell Research Laboratories.
b/ Sample MRI-79-A submitted July 1969; MRI-109-A submitted October 1969. Analyses 3-6 completed in January 1970.
c/ All entries in ppm by weight. All other elements < 5 ppm atomic except Au, Th, U not analyzed.

TABLE II

ALTERNATE IMPURITY ANALYSES OF STANDARD LITHIUM FLUORIDE SAMPLE
(Fisher CP Grade, Lot No. 74579)

Method: [a]	Emission Spec.				Atomic Absorption						Other	
	Coors		Chemo-Serv. [d]		Coors				Chemo-Serv. [d]	Willis [e]		
Analyst:	Semi-Quant. [b]	Quant. Est.	Semi Quant. [c]	Quant.							Schwarzkopf [f]	Chemo-Serv. [d]
Sample No.												
Element												
H											*	
B	< 1,000	< 1	< 10									
C											*	
N											< 20	
O												
Na	-		-	23	6,900	5,000	135.5	68.8	26	< 100		
Mg	< 1,000	1	< 100	< 1								
Al	< 1,000	300	~ 10	6	7,000	140	77.5	42.5		< 10		
Si	10^{3-4}	3,000	10^{2-3}		6,000							283
P	-		-								4	
S											120	
Cl											< 20 Hal.	
K	-		-	29	31				27			
Ca	-		-	75	7							
Cr	-		-		0.5							
Mn	-		< 100	3								
Fe	< 1,000	150	< 100	95	102							
Co	-		-	< 1								
Ni	-		-	2								
Cu	< 1,000	62	< 10	18	1							
Zn	-		< 100	30	20				35			
Sr	-		< 100 ?						< 20			
Mo	< 1,000	100	-	< 1								
Pb	< 1,000	20	< 100	8								

a/ All entries in ppm. Dash signifies sought, but not detected; blank signifies not sought.
b/ Also sought, but not detected: Be, Ti, V, Ge, Zn, Nb, Ag, Cd, Sn, Sb, Ba, Ta, Hg, Tl, Bi.
c/ Also sought, but not detected: Be, Ti, V, Ga, Ge, Rb, Zn, Nb, Rh, Ag, Cd, In, Sn, Sb, Ba, Ta, W, Pt, An, Hg, Bi.
d/ Semiquantitative emission and atomic absorption analyses performed at laboratories of McDonald-Douglas; quantitative emission analyses and Si analysis (by Wet Chemical Method) performed at St. Louis Testing Laboratories.
e/ Mr. Raymond R. Willis of Varian-Techtron, courtesy semiquantitative analysis on two samples.
f/ Sample ruined combustion tube. C, H, and O "very low" but not quantitatively determined.

TABLE III

IMPURITY ANALYSIS OF STANDARD As_2O_3 SAMPLE

(J. T. Baker Reagent Grade, Lot No. 31664)

Method		Emission Spec.				
		Coors		Chemo-Serv.		
Analyst	Spark Source Mass Spec. Bell and Howell	Semi-Quant.	Quant. Est.	Semiquant.	Other Schwarzkopf[b]	
Element[a]						
H	0.9				*	
Li	108	-		-		
B	-	< 1,000	1	-		
C	17				*	
N	1				< 20	
F	1.6					
Na	200	-		-		
Mg	-	< 1,000	60	< 10		
Al	-	< 1,000	75	-		
Si	-	< 1,000	7	< 100		
P	-	-		-	-	
S	O_2^+ interfered				< 20	
Cl	30				< 20	Hal.
K	0.7	-		-		
Cu	-	< 1,000	70	< 10		
Sb	37	-		-		

a/ All entries in ppm. Dash signifies sought, but not detected; blank signifies not sought. Elements sought were essentially the same as with LiF (see Tables I and II).

b/ Sample distilled from combustion tube. C and H "very low" but not quantitatively determined.

four successive LiF samples or on successive sparking of the same $LiAsF_6$ sample, and that of the 18 $LiAsF_6$ samples which were analyzed, the three with lowest recorded carbon contents were all loaded in the instrument at the same time. These results are summarized in Table IV.

III. EVALUATION OF SYNTHESIS METHODS

A. Previous Related Studies

The first metal salts of the hexafluoroarsenate ion were synthesized by Woolf and Emeleus who used liquid BrF_3 to fluorinate a salt[1] or oxide[2] of arsenic.

$$Ag_3AsO_4 + BrF_3(\text{excess}) \longrightarrow AgAsF_6 \cdot 2AgBrF_4$$

$$M \text{ or } MX + As_2O_3 + BrF_3(\text{excess}) \longrightarrow MAsF_6 \quad M = K^+, Ag^+, Ca^{++} \text{ or } Ba^{++}$$

These workers also used BrF_3 to prepare NO_2AsF_6[2] and $NOAsF_6$[3], the latter having been prepared over 40 years previously by the reaction of NOF and AsF_5. The reaction of 48% HF and KH_2AsO_4 to give a readily hydrolyzed $KAsF_6$, reported many years ago,[5,6] was shown by Dess and Parry[7] to give $KAsF_5OH$ instead, and who also showed that anhydrous HF was required to complete the conversion to $KAsF_6$.

$$KH_2AsO_4 + HF\ (48\%) \longrightarrow KAsF_5OH \xrightarrow[\text{anhyd}]{HF} KAsF_6$$

These workers also used BrF_3 to prepare NO_2AsF_6[2] and $NOAsF_6$[3], the latter having been prepared over 40 years previously by the reaction of NOF and AsF_5.[4] The reaction of 48% HF and KH_2AsO_4 to give a readily hydrolyzed $KAsF_6$, reported many years ago,[5,6] was shown by Dess and Parry[7] to give $KAsF_5OH$ instead, and show also showed that anhydrous HF was required to complete the conversion to $KAsF_6$.

In recent years a number of studies of hexafluoroarsenate salts of metal and nonmetal cations have been made,[8] salts of the AsF_5OH^- ion have been studied further,[9-15] salts of the $AsF_4(OH)_2^-$ ion have been discovered,[12,13] $KAsF_6$ and $HAsF_6$ have become available commercially, and $KAsF_5OH$ is available commercially in laboratory quantities. Lithium hexafluoroarsenate, however, has never been available, although it is known.

Lithium hexafluoroarsenate was first synthesized in 1956 by Cox[16] for a study of structures of several complex fluorides of the type ABF_6. The synthesis method used by Cox was that previously applied by Woolf and Emeleus[2] in the synthesis of $KAsF_6$, etc., i.e., by the action of liquid BrF_3 on a mixture of the metal halide and arsenious oxide:

TABLE IV

CARBON ANALYSIS ON $LiAsF_6$ AND LiF SAMPLES BY SPARK SOURCE MASS SPECTROMETRY

Sample No. $LiAsF_6$	Method of Preparation and Purification	Date of Analysis	Order of Analysis	Carbon (ppm)	Remarks
I-42-C	Ion exch.; cryst/aq. i-PrOH	October 28, 1969	1	304	
I-45-C	Recryst. acid; neut.; cryst/aq. i-PrOH	October 28, 1969	2	465	
I-46-D	Stock acid; neut.; recryst/aq. i-PrOH	October 28, 1969	3	309	
I-41-B	Ion exch.; evap. to dryness	October 28, 1969	1	142	
I-42-D	Ion exch.; 2nd crop/aq. i-PrOH	October 28, 1969	2	318	
I-45-D	Recryst. acid neut.; cryst/aq. i-PrOH	October 28, 1969	3	59-490	"Spotty" carbon
I-47-A	Misc. prod.; twice recryst/aq. i-PrOH	December 22, 1969	1	130	
III-20-A	Acid crystal.; neut.; dried	December 22, 1969	2	130	
III-22-A	III-20-A, recryst/aq. i-PrOH	December 22, 1969	3	88	
III-22-B	III-20-A, recryst/H_2O	December 22, 1969	1	590	"Spotty" carbon on all three samples.
III-22-C	III-20-A, recryst/Et_2O	December 22, 1969	2	540	Believed to have cellulosic impurities.
III-23-A	III-20-A, recryst/i-PrOH	December 22, 1969	3	460	May have cellulosic impurities.
I-68-A	I-66-A (acid/dried); recryst/Et_2O	February 6, 1970	1	780	
I-69-B	I-51-C (mixed products; recryst/aq. i-PrOH) recryst/Et_2O		2	2,000	Residual Et_2O?
III-44-B	I-66-A recryst/i-PrOH		3	420	
I-96-A	Acid neut. 3x recryst/H_2O	March 19, 1970	1	880	
I-96-(A)B	Acid neut. 3x recryst/H_2O	March 19, 1970	2	440	
I-96-(A)B	Sample submitted above	April 3, 1970	1	490	Successive analyses on same sample.
			2	180	1 and 3 at 16 kv.; 2 and 4 at 24 kv.
			3	180	exposure
			4	160	
Sample No. LiF					
MRI-79-A	Fisher CP grade	August 8, 1969	1	1,200	
MRI-109-A	Lot No. 74579	October 23, 1969	1	378	
MRI-109-A		January 14, 1970	1	580	
MRI-109-A		January 14, 1970	2	540	
MRI-79-A		January 14, 1970	1	300	
MRI-79-A		January 14, 1970	2	230	

$$12\ LiF + 6\ As_2O_3 + 20\ BrF_3 \longrightarrow 12\ LiAsF_6 + 10\ Br_2 + 9\ O_2$$

However, the low arsenic analysis reported by Cox suggests that the product contained considerable unreacted LiF, i.e., a composition of about $LiAsF_6 \cdot 0.4\ LiF$. The same synthesis method was later used by Kemmitt, Russell and Sharp[17] (who continued structural studies on ABF_6 salts), but these workers did not report an analysis on their $LiAsF_6$. They did note that the analogous synthesis of $LiPF_6$ always gave a product containing excess LiF. Atkinson and Hallada[18] prepared a small amount of $LiAsF_6$ for electrical conductivity studies by the ion exchange reaction:

$$KAsF_6 + Li^+ \text{ (Dowex 50)} \longrightarrow LiAsF_6 + K^+ \text{ (Dowex 50)}$$

These workers reported that $LiAsF_6$ was recrystallized and readily dried at 110° to give an anhydrous, nonhygroscopic product. Sensitive qualitative tests showed no other cationic or anionic impurities. More recently, investigators at Honeywell[19] and at Monsanto[20] have prepared methyl formate solutions of $LiAsF_6$ by the metathetical reaction:

$$KAsF_6\ (HCOOCH_3\ \text{soln.}) + LiBF_4 \xrightarrow[\text{Filter}]{30\ \text{min}} KBF_4 + LiAsF_6\ (HCOOCH_3\ \text{soln.})$$

However, the $LiAsF_6$ could not be recovered from methyl formate without decomposition. The metathesis reaction was then performed in liquid ammonia and a solvent-free product was obtained[21] which, however, like the methyl formate solution[22] may have contained KBF_4.

Finally, studies at Midwest Research Institute in early 1969 showed that LiF and AsF_5 did not react at -80° or 25°C, but underwent partial reaction upon heating.

$$LiF + AsF_5 \xrightarrow[4\ \text{days}]{178°} LiAsF_6\ (18.5\%)$$

(The rapid direct reaction of KF and PF_5, even at 500°, was reported in 1930,[5] but in the analogous preparation of $LiPF_6$, the use of a solvent such as HF,[17] dimethyl formamide, propylene carbonate or acetonitrile has been preferred.)

These reactions appear to be the only reported syntheses of $LiAsF_6$ and no other physical properties of $LiAsF_6$ appear to be known (except for some electrochemical properties). However, many similarities have been noted between the physical properties of the perchlorate salt of a given cation and its tetrafluoroborate and hexafluoroarsenate salts. Hence, $LiAsF_6$ was expected to resemble $LiClO_4$ in many properties. The $LiClO_4$ was reported to

melt at 236°C, to be very soluble in water (a saturated solution is ~ 5.6 M at 25°C) and in several nonaqueous solvents and to form the hydrates, $LiClO_4 \cdot 3H_2O$ (m.p. 95°C) and $LiClO_4 \cdot H_2O$. The $LiBF_4$ has been reported[24] to have a small dissociation pressure at 25°C and *in situ* preparation has been used,[22,24] but strangely enough, workers at Honeywell stated that they vacuum dried at 150°C the $LiBF_4$ used to prepare $LiAsF_6$.

B. Selection of Synthesis Methods

Rather surprisingly the preparation of $LiAsF_6$ by neutralization of $HAsF_6$ had not been reported, but the ready availability of $HAsF_6$ and LiOH made this method an obvious first choice. Our second choice was the ion exchange method, since this appeared to be the only method reported in the literature by which a reasonably pure $LiAsF_6$ had apparently been made and the arsenic source, $KAsF_6$, was readily available. The third choice was the reaction of LiF with AsF_5 since the LiF could be obtained in high purity and gaseous AsF_5 could be purified. A fourth choice utilized As_2O_5 and LiOH (or LiF) as starting materials, the fluorination to $LiAsF_5OH$ to be performed with 48% aqueous HF and the fluorination to $LiAsF_6$ to be completed with anhydrous HF. Methods utilizing As_2O_3 and LiF as starting materials were considered because As_2O_3 is available in higher purity than any other arsenic compound, but the required use of BrF_3[16,17] or SF_4 (which has been used[23] to prepare $KAsF_6$) to complete the reaction appeared to have severe disadvantages from the viewpoint of operational procedure and expected product purity. A summary of available starting materials is shown in Table V, and the synthesis methods are summarized by the following reactions:

1. Acid Neutralization Method

$$HAsF_6 \text{ (aqueous)} + LiOH \longrightarrow LiAsF_6$$

2. Ion Exchange Method

$$KAsF_6 + Li^+(\text{Dowex-50}) \xrightarrow[\text{Exchange}]{\text{Ion}} LiAsF_6 + K^+(\text{Dowex-50})$$

3. Reaction of AsF_5

$$LiF + AsF_5 \xrightarrow{\text{Solvent}} LiAsF_6$$

4. Reaction *via* $LiAsF_5OH$

$$As_2O_5 + LiOH \xrightarrow{H_2O} LiH_2AsO_4 \xrightarrow[48\%]{HF} LiAsF_5OH \xrightarrow[\text{anhyd.}]{HF} LiAsF_6$$

$$\text{(or) } As_2O_5 + LiF + HF \text{ (48\%)} \longrightarrow LiAsF_5OH \xrightarrow[\text{anhyd.}]{HF} LiAsF_6$$

TABLE V

AVAILABILITY OF STARTING MATERAILS

Chemical	Source	Grade	Approximate Price
$HAsF_6$	Ozark Mahoning	ca. 65% aq. solution	$46/gal (16 lb.)
$HAsF_6$	Ozark Mahoning	ca. Hexahydrate crystals	$46/gal (16 lb.)
$KAsF_6$	Ozark Mahoning	98% min.	$15/lb
AsF_5	Ozark Mahoning	Purified gas	$50/50 g.
As_2O_5	J. T. Baker	Reagent, 99.3%	$4.00/lb
As_2O_3	J. T. Baker	Reagent, 99.99%	$10/lb
H_3AsO_4	Baker and Adamson	Reagent, 99.9%	$3.50/lb
$KAsF_5OH$	Alpha Inorganics	--	$60/100 g.
$LiOH \cdot H_2O$	Matheson, Coleman and Bell	Reagent (est. $\geq$ 99.9%)	$5.50/lb
LiF	Baker and Adamson	Reagent	$8.00/lb
Li_2CO_3	J. T. Baker	Reagent 99.2%	$6.00/lb
LiCl	J. T. Baker	Reagent, 99.0%	$6.50/lb
HF	Matheson	Anhydrous, 99.9%	$2.50/3/4 lb. (lecture bottle)
HF	Matheson	Reagent, 48% aq.	$2.30/lb
BrF_3	Matheson	Purified, 98.0% min.	$13/lb
Dowex-50W-X8 (Ion exchange resin)	J. T. Baker	"Reagent"	$27/lb (no longer available)
Dowex-50W-X8 (Ion exchange resin)	Dow Chemical	--	Courtesy sample

C. Experimental Results

1. Acid Neutralization Method

$$HAsF_6\ (aq.) + LiOH\ (aq.) \longrightarrow LiAsF_6 + H_2O$$

The conversion of $HAsF_6$ to $LiAsF_6$ had never been reported previously, but was demonstrated very early in this program. The method was not, however, without problems and a series of neutralization runs were made to determine the optimum neutralization and recovery procedures and to prepare several batches of crude $LiAsF_6$ for purification studies. In all, 19 runs were made with various conditions and analyses of the products before making $LiAsF_6$ at the 2,000 g. scale. The more significant of the details of these runs will be reported here and the procedure which was finally used is well described in Section IV.

Two particular discoveries during the development of the method should be noted. First of all, the $HAsF_6$ as it is obtained commercially or even after recrystallization is not pure. The properties of $HAsF_6$ are described in more detail in Section V. The most significant impurity appears to be the heretofore unknown acid $HAsF_5OH$ most of which hydrolyzes to produce LiF and the lithium arsenates LiH_2AsO_4, and Li_2HAsO_4, during neutralization with LiOH, although complete hydrolysis apparently occurs only when the $LiAsF_6$ solution is concentrated. The solubility of the arsenates particularly is detrimental to the recovery of high purity $LiAsF_6$. One effect of the presence of the $HAsF_5OH$ is that about twice as much LiOH solution is required for neutralization as expected from the weight of the $HAsF_6$ used. A second discovery was that contrary to a literature report that anhydrous $LiAsF_6$ was not hygroscopic,* we found that $LiAsF_6$ was in fact quite hygroscopic and even deliquescent at 35% relative humidity. Further, it forms a monohydrate, which resembles the anhydrous salt in appearance, and also a trihydrate. The latter, however, was found to be particularly useful for recrystallization from water or aqueous alcohol. The properties of $HAsF_6$ and $LiAsF_6$ are described further in Section V.

Run No. 1: One hundred milliliters of greenish stock 65% $HAsF_6$ was neutralized by the addition of 5 M LiOH at 0-28°C. The mixture was cooled to -5°C and filtered. The insoluble by-product (32.9 g. dried in dry air) was extracted with acetone, but 25.7 g. remained undissolved (Found 54.2% F). The aqueous solution was evaporated to dryness on the flash evaporator at 85°C giving a very hard solid. The solid was extracted with methanol leaving 16 g. of an arsenate fraction (Found 5.9% F). The methanol and acetone extracts were combined and the solvent removed under vacuo. The solid product was dried in dry air to give 90.9 g. of $LiAsF_6 \cdot H_2O$. Lot I-6-A, Found: 3.21% Li; 35.21% As; 53.08% F; 0.89% H. (Calculated formula: $Li_{1.00}As_{1.02}F_{6.03} \cdot 0.97\ H_2O$). Carbon content was only 230 ppm.

* The salt was recrystallized from water and dried at 110°C in vacuo.

Semiquantitative emission spectrographic analysis for 34 metallic elements indicated that only Na was above 100 ppm. This product, which was slightly off-white in color, showed a strong endotherm at 116°C upon differential thermal analysis, but appeared to undergo partial decomposition upon attempted drying at ~ 110°C.

Run No. 2: One hundred milliliters of 5 M LiOH was neutralized at up to 50°C by the addition of stock 65% $HAsF_6$ (30 ml. required) and the insoluble material was filtered off. The solution was evaporated under vacuum below 40°C to near dryness and then dried in dry air to give 26 g. of white solid, Lot I-8-B. Elemental analysis indicated $LiAsF_6 \cdot H_2O$ contaminated with ~ 1% LiF and ~ 4% lithium hydrogen arsenate. (Subsequently, dehydration was completed in the lyophylizer and the product was used to test ethyl ether as an extracting solvent. The ether extracted 97% of the solid and $LiAsF_6$ was recovered; Found: 58.1% F.) Semiquantitative emission spectrographic analysis on the crude Lot I-8-B showed that of the 34 elements sought only Sb and Na were above the 100 ppm level.

Run Nos. 3 and 4: These runs were variations of Run No. 1. In Run No. 3, 100 ml. of stock, 65% $HAsF_6$, was diluted to 1,900 ml. (i.e., ~ 0.34 M) before neutralization, to determine if species present, because of the high concentration of the $HAsF_6$, were responsible for the formation of insoluble by-product and consumption of excess LiOH. Neutralization at 28°C required almost exactly the same amount of LiOH as in concentrated solution, however, and appeared to give about as much by-product; the dark green color and the slightly smaller amount (14.1 g. dried) of the recovered insoluble matter indicated that some additional white solid of low solubility was merely left in the large volume of solution. No attempt was made to recover the $LiAsF_6$.

In Run No. 4,100 ml. of stock 65% $HAsF_6$ in 100 ml. H_2O was treated with an amount of LiOH (0.6 mole) calculated to bring the solution to pH 2.5-3.0 (acid-base titration of a diluted $HAsF_6$ had shown a first end point here). The insolubles (5.8 g., nearly white) were removed and the solution concentrated. The concentrate retained the green color, but deposited white crystals upon cooling. Two crops of crude $LiAsF_6$ crystals were recovered, but a third crop obtained at 0°C melted upon warming to 25°C and appeared to be or to contain $HAsF_6 \cdot 6H_2O$, a result of incomplete neutralization.

Run No. 5: In this run, 100 cm^3 of $HAsF_6 \cdot 6H_2O$, obtained by doubly recrystallizing the 65% $HAsF_6$ solution, was neutralized at 17-25°C. Insoluble by-product still formed, however, but after its removal about 90 g. of hydrated crystals were recovered in four crops by successive steps of vacuum concentration at about 50°C and crystallization by cooling to 25°C or to 0°C. The hydrated crystals were redissolved in 20 cm^3 water at 40°, but only 16 g. could be recovered by filtration at 0°C. Furthermore, the

filtrate was quite acidic (pH < 0) showing that acidic impurities had been generated during product workup. The recovered crystals were vacuum dried for 20 hr. at 110°C. The product, Lot I-13-I was white. Elemental analysis (Schwarzkopf) gave: 3.65% Li; 38.13% As; 56.87% F (MRI analysis gave 56.7% F); 13 ppm H; and 14 ppm C, (total 98.65%) or a calculated formula $Li_{1.03}As_{1.00}F_{5.88}$. Analysis for As^{+5} and free fluoride gave 1.7% and 0.7%, respectively, indicating the presence of small amounts of LiF and lithium arsenate. Semiquantitative emission spectrographic analysis for 34 metals indicated that all except possibly Na were below the 100 ppm level. Differential thermal analysis of this product showed a small endotherm at 114°C (probably indicative of absorption of moisture during sample preparation) and decomposition at about 250°C.

Run No. 6: In this run, 187 g. of recrystallized $HAsF_6 \cdot 6H_2O$ was neutralized by addition to LiOH solution. The reaction mixture was worked up and several crops of hydrated crystals were obtained, combined and recrystallized from H_2O. A small amount of product believed to be of good purity was recovered and vacuum dried over $CaCl_2$ (Lot 1-16-G). Differential thermal analysis showed a very weak endotherm indicative of the monohydrate, but we were able to observe for the first time a small endotherm at about 258°C shown later to be characteristic of anhydrous $LiAsF_6$.

Runs Nos. 7, 8 and 9: Runs Nos. 7 and 9 were reruns of No. 6 while Run No. 8 used stock $HAsF_6$. The neutralized products were worked up by various procedures involving recrystallization from methanol, 95% ethanol and aqueous isopropyl alcohol. As a result of these studies, ~ 90% i-PrOH was tentatively selected as a recrystallization solvent for the hydrated $LiAsF_6$, even though the solubility was about 0.7 g/cm^3 at 6°C. A number of $LiAsF_6$ fractions and filtrates from these studies were then reworked.

Eight dried samples of $LiAsF_6$ were combined (96 g.), dissolved at 50°C in ~ 41% i-PrOH, and the solution was filtered. Fifty grams hydrated crystals were recovered at 6°C, dried in the lyophylizer for 20 hr. and then in the vacuum oven at 110°C for 20 hr. The product, Lot I-34-B (36 g.),was white (see below) but gave a strongly acidic (pH 0.5) solution when redissolved in water.

Several filtrates and crops of hydrated crystals were then combined (estimated 225 g. $LiAsF_6$). The solution was treated with Norite-A, filtered and concentrated. Isopropyl alcohol was added, the solution refiltered and 229 g. hydrated salt recovered. Recrystallization from aqueous i-PrOH gave 130 g. crystals. The dried product (Lot No. I-35-A, 97 g.) was quite gray, however, indicating the presence of an unknown impurity. The filtrates from the first crystallization and the recrystallization were both acidic (pH 0.5 and 1.6, respectively).

The two filtrates and the acidic solution from Lot I-34-B were recombined, adjusted to pH 8.7, and reworked to give 59 g. of hydrated crystals. These were recrystallized from aqueous i-PrOH and 20 g. of dried product recovered, Lot I-38-B. This material was white and its DTA showed only the 258°C endotherm between 25° and 350°C. Nevertheless it gave an extremely turbid solution when redissolved in water.

Run No. 10: In this run 356 g. recrystallized $HAsF_6 \cdot 6H_2O$ were neutralized at $\leq 20°C$. The $LiAsF_6$ was worked up by the filtration-concentration process and isopropyl alcohol was then added (50 cm^3 per 316 g. concentrated solution). A first crop of crystals (112 g.) was obtained by cooling the solution to 6°C. About 50 g. of these crystals were vacuum dried in a lyophylizer to give $LiAsF_6$, Lot I-45-C. The filtrate was reconcentrated and a second crop of 57 g. of crystals was obtained which was combined with the remaining 62 g. of first crop crystals for recrystallization. The 119 g. were then dissolved in a mixture of ~ 24 cm^3 92% v/v isopropyl alcohol and the solution filtered. Crystallization at 6°C followed by vacuum drying of the product in a lyophylizer gave 44 g. of anhydrous $LiAsF_6$, Lot I-45-D.

Complete analyses were made on Lot I-45-C and I-45-D with the results shown in Table VI, along with the analyses of two other lots discussed later. Carbon and oxygen are seen to be the only significant impurity elements and suggest the presence of carbonate and arsenate (or fluoroarsenate) species. The low H values indicate good removal of water and alcohol by the drying procedure used, i.e., only about 0.005 mm Hg and ambient temperature in the lyophylizer.

Runs Nos. 11-17: These runs were made primarily to compare the amounts of the suspected $HAsF_5OH$ present in the stock 65% $HAsF_6$, recrystallized $HAsF_6$ and doubly recrystallized $HAsF_6$. Stirred solutions of lithium hydroxide were neutralized dropwise with solutions of $HAsF_6 \cdot 6H_2O$. The temperature was maintained by an appropriate external ice or water bath. The course of the reaction was monitored with a glass electrode pH meter and addition of acid stopped at $\sim$ pH 10. The quantities of acid added were determined. The reaction mixtures were filtered to collect insoluble materials, which were then washed with water and air dried. The experimental conditions and results are summarized in Table VII.

The solutions from Runs Nos. 11 and 12 were combined, after removal of the insolubles, concentrated, 90% i-PrOH added (15 cm^3/80 g. concentrate), and additional insolubles removed. Crystallization at 6°C, followed by vacuum drying of the crystals gave 22 g. of anhydrous $LiAsF_6$, Lot I-46-D; analysis of this product is shown in Table VI.

TABLE VI

ANALYSIS OF $LiAsF_6$ SAMPLES PREPARED BY ACID NEUTRALIZATION AND CRYSTALIZED FROM AQUEOUS ISOPROPYL ALCOHOL

Prep. Method:	Recryst. $HAsF_6$ + LiOH		Stock Acid + LiOH	Misc. Prod.
	Cryst.	Recryst.	Cryst.	Twice Recryst.
Lot No.:	I-45-C	I-45-D	I-46-D	I-47-A
Major Constituent[a] Analysis (in %) (Schwarzkopf)				
Li	3.32	3.42	3.35	3.25
As	38.47	38.08	38.31	38.43
F	57.97	58.45	58.44	57.80
Total	99.76	99.95	100.10	99.48
Li/As/F	0.93/1.00/5.95	0.97/1.00/6.02	0.91/1.00/5.93	0.92/1.00/5.84
Arsenic and Fluoride Impurity Analysis (in %) (MRI)				
As(V)		ND	tr ?	
As(III)	ND	ND		
Free F^-	ND	ND	ND	ND
Spark Source Mass Spectrometric Analysis (in ppm)(Bell and Howell)				
Order of Sample Analysis	2	6	3	b/
H[c]	10	13	2	13
B	6	-	8	7.1
C[c]	465	59-490	309	130
N	17	2	3	17
O	914	425	379	1,400
Na[d]	272	160	300	89
Mg	21	21	-	-
Al	11	2	-	-
Si	-	-	19	3
P	-	-	-	-
S	35	56	10	-
Cl	84	19	9	29
K[d]	351	367	543	34
Ca	13	52	-	7.2
Ti	12	6	-	2
Cr	-	6	-	-
Fe	-	8	-	-
Ni	14	22	6	5
Cu	-	-	-	-
Zn	-	85	-	-
Sb	15	-	-	-

TABLE VI (Concluded)

Prep. Method:	Recryst. $HAsF_6$ + LiOH		Stock Acid + LiOH	Misc. Prod.
	Cryst.	Recryst.	Cryst.	Twice Recryst.
Lot No.:	I-45-C	I-45-D	I-46-D	I-47-A
Atomic Absorption Analysis (in ppm) (Coors)[d/]				
Na	26; 35	ND (< 5); 40	51	-
K	78; 94	17	87	-

a/ Analysis of Lot I-45-D by Galbraith Labs gave: 3.40% Li; 38.13% As and ~57% F. Theoretical for $LiAsF_6$: 3.54% Li; 38.25% As; 58.21% F.

b/ Samples mounted in groups of three. Numbers 1, 4 and 5 were Lots I-42-C, I-41-B and I-42-D, respectively. Lot I-47-A was mounted with Lots III-20-A and III-22-A and was first analyzed.

c/ Schwarzkopf reported 0.10% H and 0.14% C on Lot I-45-C. Mass spectrometry results on I-45-D varied on successive exposures.

d/ High Na and K from cross contamination with ion exchange samples. Second AA values for Lot I-45-C from Schwarzkopf and for Lot I-45-D from Galbraith.

TABLE VII

ANALYSIS OF $HAsF_6 \cdot 6H_2O$ FRACTIONS FOR $HAsF_5OH$

Run No.	11	12	13	14	15	16	17
$HAsF_6$ used	Crude	Crude	Crude	1st ML	1st xtals	2d ML	2x xtals
Wt. (g.)	53	54	54	21	45	44	57
H_2O (cc.)	26	25	0	0	22	0	25
Temp. (°C)	10	40	10	10	10	10	10
$LiOH \cdot H_2O$ (g.)	20	20	20	10	10	10	10
H_2O (cc.)	100	100	100	50	50	50	50
Insol. (g.)	10	12	10.5	5	3.5	4.7	0.5
% $HAsF_5OH$ (calc.)	--	--	12.6	15.7	4.9	5.4	0.5

Lot No. I-47-A: Several assorted lots of $LiAsF_6$ and $LiAsF_6$ solutions were combined, adjusted to pH 10, treated with Norite A and filtered. The solution was then concentrated, treated with i-PrOH and 241 g. of hydrated crystals recovered. These were recrystallized from aqueous i-PrOH (174 g. recovered) and dried to give 128 g. of product. Elemental analysis and spark source mass spectrometric analysis reported in Table VI show that this material was of only moderate purity.

Lot No. I-51-C: Six assorted filtrates from previous $LiAsF_6$ crystallizations were combined, adjusted to pH 10.6 and reworked by the filtration, concentration, crystallization procedure. Two crops of hydrated crystals (246 g. total) were recovered, recrystallized (153 g.) from aqueous i-PrOH and dried to give 116 g. of product. Elemental analysis gave: 3.31% Li; 38.08% As; 58.70% F (total 100.09%). This product, however, gave a positive test for free fluoride ion (trace) and gave a turbid saturated solution.

Run No. 18: In this run a new batch of hexafluoroarsenic acid crystals obtained from Ozark Mahoning (Lot No. R-4-90) was used for the first time. This run was intended to evaluate some modifications of the neutralization and recovery procedures and also to compare water, isopropyl alcohol and ethyl ether with aqueous isopropyl alcohol as recrystallization solvents.

The procedural modifications were designed to reduce levels of the suspected impurities of carbonate, as well as arsenate, fluoroarsenates, or fluoride in previous samples. In order to reduce carbonate, the LiOH was made up as a concentrated ($\sim$ 5 M) solution, allowed to stand to precipitate any Li_2CO_3 and then filtered. The LiOH solution was maintained in a plastic

dropping funnel and added to the stirred $HAsF_6$ solution (298 g. crystals in 70 ml. H_2O) contained in a plastic beaker (all previous runs except Nos. 1, 3, and 4 had employed the reverse addition, thus exposing the LiOH solution to atmospheric CO_2). In an effort to reduce the arsenate-type of impurities, the neutralized solution was heated 1 hr. at 55°-60°C to try to complete the hydrolysis of unstable species (such as $LiAsF_5OH$), chilled to 0°C to minimize the solubility of by-products (such as LiF and Li_2HAsO_4), and then filtered.

The neutralization of the new $HAsF_6$ crystals required about the same amount of "excess" LiOH and gave about the same amount of insolubles (47.6 g., dry) as did the 65% solution. (The LiOH addition was inadvertently continued to pH 10-11 and was readjusted back to pH 7.3 with $HAsF_6$ solution after heating). The $LiAsF_6$ was recovered by two flash distillation-crystallization steps, the two crops combined, and then dried to give 138.1 g. (70.5% yield based on the weight of $HAsF_6 \cdot 6H_2O$) of Lot III-20-A. Elemental and impurity analyses of this material are shown on page 22. A concentrated solution of this material was turbid and, in time, a slight precipitate formed.

Portions of Lot III-20-A were recrystallized from each of the four solvents. The conditions used and recoveries obtained are shown in Table VIII.

Elemental and impurity analyses for these four lots are shown in Table IX. The analytical results indicate that Lot III-20-A had a purity of about 99.8-99.9%. Carbon levels were reduced,but to only 130 ppm and the oxygen level (520 ppm) was about the same as in earlier samples. The high Sb level (500 ppm) was never observed in recrystallized samples. Analytical data on Lot III-22-A (recrystallized from aqueous i-PrOH) show only 340 ppm oxygen as a significant impurity. A concentrated solution of this lot gave little, if any, turbidity. The $LiAsF_6$ recrystallized from water (both crops) also gave only very faint positive turbidity test. Unfortunately the spark source mass spectrometer analysis on Lot III-22-B did not give reliable values for C and O because of cross contamination from Lots III-22-C and III-23-A. The contamination in these two appears to be cellulosic materials dissolved from the capliner of the screw-cap bottles used to equilibrate the salt and anhydrous solvent, thus accounting for the high H, C, and O levels. Lot III-22-C (from ether) gave a very turbid aqueous solution while Lot III-23-A gave a slight turbidity.

Run No. 19: The purposes of this run were similar to those of Run 18, using a larger scale. The neutralization and recovery procedures were similar except that the concentrated $LiAsF_6$ solution was filtered to remove about 0.5 g. of insoluble material before crystallization. From 596 g. of acid crystals, 252 g. (64.3% yield based on weight of $HAsF_6$) of anhydrous $LiAsF_6$ was recovered (Lot I-66-A), along with 102 g. of insoluble by-product.

TABLE VIII

RECRYSTALLIZATION OF LOT III-20-A, $LiAsF_6$

Recry. Solvent[a]	Vol. Solvent (ml.)	Wt. $LiAsF_6$ (g.)	Recry. Temp. (°C)	Recovered Crystals (g.)	$LiAsF_6$ (Dry) (g.)	Percent Recovered	Product Lot No.
68.5% v/v i-PrOH	29.2[b]	25	-50	16.6	11.0	44	III-22-A
H_2O	25.0	50	0	23.1	17.0[d]	34	III-22-B
	2nd Crop		0	14.2	10.5	21	III-23-B
i-PrOH	40.0[c]	25	-50	5.3	4.5	18	III-23-A
Et_2O	50.0	25	-50	10.9	6.2	25	III-22-C

a/ All samples were equilibrated at 30°C overnight, then filtered before cooling to crystallize.

b/ The amount of H_2O is just sufficient to give a 1:4 ratio of $LiAsF_6$ to H_2O.

c/ This volume was too large and part had to be evaporated to recover any product.

d/ Weight losses correspond to compositions of $LiAsF_6$ to solvent of: 1:3.9 and 1:3.84 for H_2O; 1:0.58 for i:PrOH and 1:2.0 for Et_2O.

TABLE IX

ANALYSIS OF $LiAsF_6$ SAMPLES RECRYSTALLIZED FROM DIFFERENT SOLVENTS

Prep. Method	Acid Neutral. Dried	Recrystallized III-20-A (Solvent Indicated)			
		Aq. i-PrOH	H_2O	Et_2O	i-PrOH
Lot No.	III-20-A	III-22-A	III-22-B	III-22-C	III-23-A
Major Constituent Analysis (in %) Schwarzkopf[a/]					
Li	3.36	3.29	3.32	3.33	3.34
As	37.95	38.05	38.04	38.10	38.11
F	57.80	58.40	57.94	57.74	58.13
Total	99.11	99.74	99.30	99.17	99.58
Li/As/F	0.96/1.00/ 6.00	0.93/1.00/ 6.04	0.94/1.00/ 6.00	0.94/1.00/ 5.97	0.95/1.00 6.01
Mass Spectrometric Analysis (in ppm) Bell and Howell					
Order of Anal.[b/]	2	3	4	5	6
H	8.2	3.1	15	450	36
B	2.2	1.7	2.9	3.1	3.8
C[c/]	130	88	590	540	460
N	16	14	20	14	33
O[c/]	520	340	450	1,600	850
Na	120	120	88	44	22
Al	-	-	0.7	1	1
Si	23	68	47	84	130
S	10	72	16	51	25
Cl	3	17	9.9	67	41
K	22	59	14	34	70
Ca	-	2	-	3.3	2
Cr	3	2	2	2	3.2
Ni	14	-	5.7	-	9.8
Sb	500	-	-	-	80
Na Analysis (in ppm) Schwarzkopf					
Na	35	17	14	24	106

a/ Analysis of III-20-A by Galbraith Labs. gave 3.44% Li; 38.48% As; ~ 56% F; and 35 ppm Na. Theoret.: 3.54% Li; 38.25% As; 58.21% F.

b/ First sample analyzed was Lot I-47-A.

c/ Spotty C and O conc. on Samples 4, 5, and 6. Cellulosic impurities in Lots III-22-C and possibly III-23-A believed to be responsible.

The Lot I-66-A material gave a slight positive turbidity test, but was not further analyzed. It was believed to be of about the same purity as (or better than because of the extra filtration step) Lot III-20-A. One hundred gram portions of Lot I-66-A were used to retest anhydrous isopropyl alcohol and ethyl ether as recrystallization solvents. All but about 2 g. of the 100-g. $LiAsF_6$ was dissolved in 180 ml. ether at 40°C. The solution was filtered, cooled to -20°C and then 128.1 g. of $LiAsF_6 \cdot 2Et_2O$, was recovered (73% recovery, unsolvated basis). The solid was placed in the lyophylizer and pumped on to remove the ether. Considerable difficulty was encountered during the first portion of this procedure because the ether evolved so rapidly and the unsolvated product was of such fine particle size that a fine dust was carried out of the tall beaker container. The pumping was continued for about 48 hr. and 60.4 g. of product, Lot I-68-A, was recovered. The material gave a fainter turbidity test than did the starting material, but still slightly positive. This product appeared to be of much smaller particle size than those obtained from aqueous solution.

The 100 g. of Lot I-66-A was almost completely dissolved by 135 ml. alcohol. The solution was filtered and cooled to -20°C. The solid which formed, melted upon attempted recovery, however. Extensive flash evaporation of the solution at temperatures up to 70°C was required to get a good recovery of solid. Filtration of the concentrated slurry at room temperature yielded 61.8 g. of unsolvated $LiAsF_6$ which dried overnight in the lyophylizer to a final weight of 59.2 g., Lot III-44-B. This material gave only an extremely faint turbidity test, and was of more coarse particle size than that from ether.

Spark source mass spectroscopic analyses on Lots I-68-A and III-44-B are shown in Table X together with the analysis of another batch of $LiAsF_6$, Lot I-69-B, which was submitted at the same time and loaded in the mass spectrometer together with the two lots above. Lot I-69-B was a product also obtained by recrystallization from ether (see below). Unfortunately, Lot I-69-B contained an exceptionally large amount of hydrogen and carbon, suggesting that removal of the ether was incomplete. The C, H, and O values are therefore suspect for the other two lots because of the possibility of cross contamination, but indicate a mixture of several species containing H, C or O. The chlorine value for Lot I-68-A is the largest observed in any of our $LiAsF_6$ samples, but appears to be real since the other two lots recrystallized from ether (Lot III-22-C and I-69-B) were also fairly high in Cl.

Lot I-69-B: This product was obtained in 38.6 g. yield (55%) by recrystallizing 70 g. of Lot I-51-C from ethyl ether. The ether of solvation was allowed to evaporate in a stream of dry air to avoid the difficulties previously encountered in removing this ether in vacuo. After 3 days, loss of 2 moles of ether per $LiAsF_6$ was indicated and the product was then

TABLE X

ANALYSIS OF $LiAsF_6$ RECRYSTALLIZED FROM ANHYDROUS ISOPROPYL ALCOHOL AND ETHYL ETHER

Lot No. $LiAsF_6$	I-68-A	III-44-B	I-69-B
Starting Material	Lot I-66-A (Acid Neut., Dried)		Lot I-51-C
Recrystallized Solvent	Et_2O	i-PrOH	Et_2O
Order of Analysis	1	3	2
H[a/]	53	26	150[b/]
B	0.88	0.3	0.93
C	780	420	2,000[b/]
N	11	1.6	7.4
O	630	400	370
Na	25	20	64
Si	5	3	49
S	11	11	84
Cl	140	46	84
K	11	24	56
Ca	5.1	2	5.7
Fe	14	-	59

a/ All entries in ppm by weight. All other elements < 5 ppm.

b/ Apparently residual ether in Lot I-69-B. The C and H values for Lot I-68-A and Lot III-44-B may be high because of cross contamination.

pumped on in the lyophylizer for 3.7 hr. The product, Lot I-69-B, gave a negative turbidity test. The impurity analysis is shown in Table X and discussed in the preceding paragraph. The particle size was not nearly so fine as that obtained when the ether was removed in vacuo, i.e., Lot I-68-A.

The recurring development of small amounts of white solid or turbidity during concentration of $LiAsF_6$ solutions, and the pH drift to the acidic side raised the possibility that the AsF_6^- itself was hydrolyzing. Therefore, a thermal stability test was made. One gram of Lot I-69-B was placed in a glass tube and dissolved in distilled water. The clear solution was frozen, the tube evacuated and sealed off. After 1 hr. at 100°C no turbidity could be detected in the solution.

Conclusions on acid neutralization method: Commercial $HAsF_6$ solution or hydrated crystals can be converted to $LiAsF_6$ and a product of good purity can be recovered in 60-70% yield, after separation from by-products of low solubility. Pre-purified $HAsF_6$ gives less by-product and better yields, but the recovery of $LiAsF_6$ is not simplified significantly, i.e., all the impurities can be removed from the $LiAsF_6$ more easily than from $HAsF_6$. All hydrolytically unstable species must be destroyed during product recovery and control of pH at about 8 is important. The product can be recovered and recrystallized as $LiAsF_6 \cdot 3H_2O$ and then dried in a lyophylizer to anhydrous $LiAsF_6$.

2. Ion Exchange Method

$$KAsF_6 + Li^+ \text{ (Dowex-50W)} \xrightarrow[\text{Column}]{\text{Ion Exchange}} LiAsF_6 + K^+ \text{ (Dowex-50W)}$$

The literature report of the preparation of $LiAsF_6$ by the ion exchange method does not give details on the conditions used, but apparently a small batch process was employed. We have made three preparations of $LiAsF_6$ using ion exchange columns of increasingly large capacity. The cation exchange resin, Dowex 50W-X8 (50-100 mesh) was obtained from two sources: a "reagent" grade obtained from J. T. Baker Chemical Company (stated to have an exchange capacity of 1.9 meq/ml, wet volume, and 5.0 meq/g dry basis with a moisture content of 52.5%); and a courtesy sample from the Dow Chemical Company. Both samples were obtained in the acid form.

First run: One hundred grams of resin (J. T. Baker), capacity 238 meq., was converted to the lithium form by standing overnight in LiOH solution, 250 meq. (final pH: 8.6) and then added to a 1 in. I.D. column to give a depth of 32 cm. Potassium hexafluoroarsenate, 237 meq., 54 g. (Ozark Mahoning Company, Lot KW-4-100), was dissolved in 250 cm^3 H_2O (i.e., ~0.96 M), passed onto the column at a rate of 0.104 cm^3/cm/min and then followed with 50 cm^3 H_2O. Fractions of about 20 cm^3 each were collected and semi-quantitatively analyzed for Li^+ and K^+ by flame photometry. The exchange was not nearly complete and K started eluting at fraction 16 along with the Li. Fractions 3-15 were combined (fractions 1 and 2 were discarded since the small Li

level may have arisen from LiOH) and the liquid removed under vacuo to give 44 g. of hydrated crystals. These were redissolved in ~ 70% aqueous alcohol; a small amount (~ 0.4 g.) of insoluble white solid was filtered off. Hydrated $LiAsF_6$ crystals were recovered and dried in the lyophylizer at ambient temperature for about 24 hr. and then in a vacuum oven at 110°C for 20 hr. The final product Lot I-33-C (7.5-8 g.) gave the following analysis: 3.34% Li; 38.05% As; 58.54% F; 0.19% H; 0.00% C (Total: 100.12%) or a calculated formula of $Li_{0.95}As_{1.00}F_{6.10}H_{0.33}$. (The presence of the hydrogen was surprising after the prolonged drying and may indicate the presence of acidic impurities such as HF or $HAsF_6$ rather than H_2O.)

Second run: The exchange resin from the first run was regenerated with strong HCl and mixed with fresh resin to give a total of about 300 g. resin, capacity 0.71 eq. This was converted to the Li form with LiOH solution, 0.74 eq., and then added to a 1-in. column to give a depth of 83 cm. The $KAsF_6$, 0.71 eq. (162 g. in 800 cm^3 H_2O, i.e., ~ 0.8 M) passed onto the column at a rate of 0.026 cm3/cm/min and then followed with ~ 200 cm^3 H_2O. Eighteen fractions of about 60 cm^3 each were collected and checked for Li^+ and K^+. Unlike the first run, a significant amount of K^+ appeared in the third fraction and was present thereafter. All fractions were therefore combined. The solution (925 cm^3) was quite acidic, pH 3.0, and was adjusted to pH 10 with LiOH solution.

The dissolved $LiAsF_6$ was recovered by two techniques. One-third of the solution was condensed on a flash evaporator, some insoluble material was removed, and then evaporation continued to dryness to give 49 g. of the monohydrate (found 52.6% F, theoret. 53.35%), a hard solid. Further drying for 28 hr. in the lyophylizer gave a fine powder, Lot I-41-B, which was analyzed for all elements with the results shown in Table XI. On the basis of the weight of monohydrate a total recovery of about 97% $LiAsF_6$ is indicated for this ion exchange run.

The remaining two-thirds of the collected $LiAsF_6$ solution was flash evaporated to 145 g. and 1-2 g. insoluble material was removed. The addition of 25 cm^3 isopropyl alcohol and cooling the solution to 6°C produced a further 3 g. of precipitate which was removed. Two additional 25 cm^3 portions of i-PrOH were added while the solution was further concentrated to 113 g. The solvated $LiAsF_6$ crystals (32 g.) were recovered at 6°C and dried in the lyophylizer to yield 22 g. of $LiAsF_6$, Lot I-42-C. The filtrate was further concentrated to 76 g., 20 cm^3 i-PrOH added and a second crop of solvated crystals (30 g.) recovered at 6°C. Drying gave 21.5 g. of $LiAsF_6$, Lot I-42-D. Analyses of these samples are also shown in Table XI.

Third run: For this larger scale run about 800 ml. of resin was used having an estimated capacity of five equivalents. The Dow resin was washed to remove a reddish impurity (probably an acid indicator), converted to the lithium form and then mixed uniformly with the J. T. Baker resin (which had been reconverted to the Li form with saturated LiCl solution. The resin gave a height of 116 cm. in a 35 mm O.D. tube. It was given a

TABLE XI

ANALYSIS OF $LiAsF_6$ SAMPLES PREPARED BY ION EXCHANGE

Prep. Method	Evap. to Dryness	Cryst/aq i-PrOH	2nd Crop
Lot No.	I-41-B	I-42-C	I-42-D
Major Constituent[a] Analysis (in %) Schwarzkopf			
Li	3.26	3.42	3.23
As	37.82	38.28	38.33
F	58.19	58.04	58.04
Total	99.27	99.74	99.60
Li/As/F	0.93/1.00/6.07	0.96/1.00/5.98	0.91/1.00/5.97
Arsenic and Fluoride Impurity Analysis (in %) MRI			
As(V)		ND	ND
As(III)		ND	ND
Free F^-		ND	
Spark Source Mass Spectrometric Analysis (in ppm) Bell and Howell			
Order of Sample Analysis[b]	4	1	5
H	6	7	8
B	11	12	5
C	142	304	318
N	2	13	2
O	646	314	180
Na*	1,408	328	797
Mg	11	3	5
Al	18	6	2
Si	67	32	-
P	-	10	-
S	56	38	80
Cl	56	30	36
K*	4,470	4,310	559
Ca	20	13	7
Ti	11	6	6
Cr	11	-	-
Fe	-	15	-
Ni	36	21	18
Cu	-	29	-
Zn	136	13	43
Ga	-	341[c]	-
Ge	-	50	-
Se	-	42	-
In	-	234	-
Sb	1,190	-	-
Atomic Absorption Analysis (in ppm) Coors			
Na	380	179	83
K	4,170	3,630	961

a/ Theoretical for $LiAsF_6$: 3.54% Li; 38.25% As; 58.21% F.

b/ Samples mounted in groups of three, Nos. 2 and 3 were Lots I-45-C and I-45-D, respectively, and No. 6 was Lot I-46-D.

c/ The Ga, Ge, Se, and In are probably a "memory" effect. These elements were never observed in other $LiAsF_6$ samples.

final treatment with saturated LiCl solution and then washed with distilled water just before use until free of Cl^-.

A 228 g. (1 mole) quantity of $KAsF_6$ (Ozark Mahoning, Lot No. WH-1-41) was dissolved to make 2 liters solution (0.5 M) filtered to remove a small amount of insoluble material and passed through the ion exchange column at a flow rate of 3 ml/min. The effluent was collected in fractions and checked periodically until a flame test showed that no more lithium was eluting. The total volume of eluate was about 2,200 ml. Qualitative spot checks of the various fractions of eluate with a flame photometer showed that all fractions contained potassium, even the last fraction in which the lithium was low.

The fractions were therefore combined, the excess solvent evaporated and 164.4 g. of hydrated crystals (about 60% yield) was obtained by crystallization of four crops of crystals. The crystals were, however, slightly yellowish and they were, therefore, recrystallized. The recrystallization was performed by adding 5 ml. water, warming to 70°C to melt the trihydrate, and then cooling slowly to room temperature to yield a first crop of crystals and then to -10°C to yield a second crop. Both crops were very white and were combined (112.1 g.) and then dried to give 83.5 g. (Lot III-37-C) of anhydrous $LiAsF_6$, representing an overall yield of 42.6%. This product, however, had a faintly grayish color. We had previously observed this type of reaction when drying samples of $LiAsF_6$ prepared by the acid neutralization method which had been recovered from acidic solutions. The filtrates from both the first (yellowish) and second crystallizations were found to be quite acidic (pH < 0.1) and deposited insoluble materials and etched the glass flask on standing. The source of these acids may be the hydrolysis of $KAsF_5OH$ (or $LiAsF_5OH$ after ion exchange) present as an impurity in the $KAsF_6$. The yellow impurity was also observed in the large scale run of the acid neutralization method. A brief attempt was made to purify Lot III-37-C by recrystallization from ethyl ether. However, a reddish-brown coloration developed in the ether solution which hindered the recovery of high purity $LiAsF_6$ and the recrystallization was terminated.

Conclusions: The ion exchange method gave a product which was contaminated with potassium in these runs. While the potassium might be removed by further treatment with the resin or by recrystallization, the method also has the same problems with oxygenated impurities (apparently present in the starting $KAsF_6$) as the acid neutralization method. Overall the ion exchange method is much less suited to scale up than $HAsF_6$ method.

3. Reaction of LiF and AsF_5

$$LiF + AsF_5 \longrightarrow LiAsF_6$$

Our preliminary research (February 1969) had determined that this reaction did not occur appreciably at 25° in the absence of a solvent in an unstirred system, but that ~ 20% conversion was obtained after three days at 178°C. In our present study, three further runs were made with only moderate success.

First run: 3.3 g. (0.127 mole) LiF and 21.7 g. (0.128 mole) AsF_5 were combined with 5 ml. anhydrous HF in a Kel-F tube and held at -80° to -40°C for several days. The solid appeared to become crusty and shaking the tube did not effect good mixing. The volatile products were removed and the solid recovered; wt.: 9.5 g., theoretical for $LiAsF_6$ 25.0 g. (calc. for $LiHF_2$, 5.9 g.). The solid was crushed and recombined with the volatiles for several days under similar conditions. The recovered solids now weighed 13.1 g. (calc. conversion: ~45%). Efforts to extract the $LiAsF_6$ from the mixture suggested that in addition to the $LiAsF_6$ and unreacted LiF, a third material was also present which appeared to have resulted from reaction of adventitious moisture with the AsF_5 during the vacuum line manipulations. No high purity $LiAsF_6$ was recovered.

Second run: The reaction was attempted in the absence of any solvent. A valved 95 ml. Monel cylinder was prepassivated at about 100°C with a mixture of 200 mm. F_2 and 20 mm. AsF_5, then evacuated. Dried LiF (3.3 g., 0.127 mole-B&A reagent grade) was charged to the cylinder inside a drybox and the cylinder and contents then again heated briefly under vacuum. Arsenic pentafluoride (Ozark Mahoning Company) was condensed into a Kel-F measuring tube and 9.5 to 10.0 cm^3 (~ 23 g., ~ 0.135 mole) was distilled from a -63°C bath and condensed into the reactor at -196°C. The reactor was held at 200°C for 18 hr.

The volatile contents were removed (~ 5 cm^3 at -63°C) and only 6.4 g. of solid product could be recovered in the drybox without hard scraping of the cylinder walls. These results showed that the reaction had not gone to completion. The product gave an excellent infrared spectrum of a AsF_6^- salt, but had a slight pinkish color which suggested contamination by metal salts. The solid mixture was extracted with 13 ml. ethyl ether to remove $LiAsF_6$, leaving 1.8 g. of insoluble residue. Evaporation of the ether gave 4.6 g. of white solid product (Product III-26-A). Elemental analysis confirmed the identity of $LiAsF_6$; the data showed too much error (note total) to give a clear indication of purity, but suggested that some LiF was present.

	Li	As	F	Total
Product III-26-A	4.00	37.80	59.01	100.81%
$LiAsF_6$, Theoretical	3.54	38.25	58.21	

Third run: The reaction was attempted using ethyl ether as a solvent. The reactor cylinder was charged with 1.7 g. LiF and weighed. The recovered AsF_5 fraction from trial 2 ($\sim$ 5 cm^3) and 25 ml. ethyl ether were then added and the mixture let stand at room temperature overnight. After the volatile components were removed, the reactor retained 19.3 g. of nonvolatile product: i.e., much larger than theoretical (12.8 g. for $LiAsF_6$). The product was a mixture of black liquid and solid, indicating that degradation reactions had occurred between the AsF_5 and ether. (No acid-base adducts, analogous to $(C_2H_5)_2O:BF_3$, appear to be known for $(C_2H_5)_2O$ and AsF_5.) The black material was stirred with 50 ml. of water. A slight fuming occurred, but most of the material was recovered upon filtration as a gray fibrous-looking solid which was not further analyzed.

Conclusion: The LiF-AsF_5 reaction is not competitive with the acid neutralization method for the production of high purity $LiAsF_6$. The experimental procedure is more difficult and the starting material (AsF_5) is expensive. The reaction without solvent did not go to completion in the absence of stirring or grinding (the LiF crystals are likely coated with a layer of $LiAsF_6$ which retards further reaction). The two solvents tested, HF and $(C_2H_5)_2O$, were not effective under the conditions used and while satisfactory solvents probably exist, further study was not warranted.

4. Conversion of As_2O_5 via $LiAsF_5OH$

The conversion of KH_2AsO_4 to $KAsF_5OH$ by 48% HF and the conversion of the latter to $KAsF_6$ by near-anhydrous HF was demonstrated by Dess and Parry. We attempted to adapt this method to the preparation of $LiAsF_6$. Since $LiAsF_5OH$ has not been heretofore described in the literature, its synthesis, identification and characterization was the first step. The LiH_2AsO_4 is not available and As_2O_5 was utilized as the starting material. Two slightly different methods for converting As_2O_5 to $LiAsF_5OH$ were examined. The overall series of reactions by the first method are:

$$\text{I.} \quad As_2O_5 + 2LiOH + H_2O \longrightarrow 2\ LiH_2AsO_4$$

$$\text{II.} \quad LiH_2AsO_4 + 5HF\ (48\%) \xrightarrow{100°C} LiAsF_5OH + 3H_2O$$

$$\text{III.} \quad LiAsF_5OH + HF\ (100\%) \longrightarrow LiAsF_6 + H_2O$$

Alternatively, an attempt was made to convert the As_2O_5 directly to $LiAsF_5OH$ according to the equation:

$$2LiF + As_2O_5 + 8HF\ (48\%,\ \text{excess}) \xrightarrow{100°C} 2\ LiAsF_5OH + 3H_2O$$

Attempted preparation of $LiAsF_5OH$ via LiH_2AsO_4:

First run: A suspension of 115 g. As_2O_5 in 200 ml. H_2O was prepared and a solution of 42 g. $LiOH \cdot H_2O$ in 200 ml. H_2O was added in small portions while stirring. The cloudy mixture was heated and stirred at 70° for 1 hr. Final pH = 4.7. The solution was filtered and chilled but no solid products were obtained. The solution was evaporated on the vacuum concentrator to 210 g. On standing, some solid crystallized, but the bulk remained fluid. The entire mass was transferred to a polyethylene (PE) beaker, 200 ml. 48% HF added and the mixture heated on the steam bath for three days. An additional 100 ml. 48% HF was added and evaporation continued on the steam bath an additional 16 hr. The mixture was cooled in a refrigerator overnight, but no crystalline product was obtained and heating was continued on the steam bath for 8 hr. The resulting fluid contained in a PE bottle crystallized on chilling in the refrigerator. A small quantity of mother liquor was removed by suction filtration. The hydrous-looking solids were treated with 25 ml. isopropanol at 60°. Undissolved materials (23 g. air dried) were filtered and the filtrate was stored in the refrigerator. The crystallized product was collected (65 g.) and redissolved in 22 ml. 90% isopropanol. Some white solids remained undissolved. On standing in the refrigerator no further products crystallized. The white solid (10 g. air dried) was removed and the filtrate evaporated in the vacuum concentrator, at 60° bath temperature. Evolution of gaseous materials indicated some apparent reaction or decomposition. The concentrated liquid (50 g.) was cooled in the refrigerator, but only a small quantity of crystals developed. Further attempts to recover the product were unsuccessful.

Second run: A suspension of 115 g. (0.50 mole) of As_2O_5 in 200 cm^3 H_2O was reacted with a solution of 42 g. (1.00 mole) $LiOH \cdot H_2O$ in 200 cm^3 H_2O. The mixture was heated at 70°C for 1 hr. and filtered to remove suspended material. The filtrate was flash evaporated at 55°C until the LiH_2AsO_4 was a viscous white mass (wt. 158.9 g.; theoret. 147.9 g. for anhydrous LiH_2AsO_4). About 150 g. of this material was transferred to a polyethylene beaker, 200 cm^3 of 48% HF ($\sim$ 5.5 moles) was added, and the mixture heated on a steam bath overnight to convert the LiH_2AsO_4 to $LiAsF_5OH$. The reaction mixture was filtered and 27.2 g. of pinkish solid recovered, leaving 143.1 g. filtrate.

The solid was dried in a dry air stream with occasional crushing for one week to a final weight of 24.8 g. (Product I-61-C). Analysis gave: 14.40% Li; 20.35% As; 43.71% F (total 78.46%). The atomic ratios, $Li_{1.00}As_{0.13}F_{1.11}$, and the very low solubility in water suggest that this product contains much LiF (the maximum amount of LiF which could be formed is 25.9 g., based on the LiOH used) and probably an arsenate.

The filtrate was cooled but no solid separated. It was then evaporated in a dry air stream until a large amount of solid separated. Filtration gave 87.6 g. of solid which was further dried in an air stream to about 70 g. and then under vacuum to a final weight of 60.9 g. (Product I-61-D). This slightly gray product was not the desired $LiAsF_5OH$ as shown by the low fluoride analysis. (Found: 18.5% F.) It probably contains much arsenate.

Attempted direct conversion of As_2O_5 to $LiAsF_5OH$:

First run: The LiF (0.258 mole, 6.68 g., B&A reagent grade) and As_2O_5 (0.129 mole, 29.65 g., J.T. Baker reagent grade) were combined with 60 ml. of 48% HF (J.T. Baker reagent grade) (1.66 moles HF) in a polyethylene bottle and heated at 75° and 100°C for 2 hr. each. The mixture was then dried over the weekend in a dry air stream. The resulting product was inhomogeneous, consisting of a large crystalline mass and a white paste which appeared to be unreacted As_2O_5. The product weighed 55.5 g. compared to 50 g. theoretical, suggesting that the reaction had occurred to a significant extent. The crystalline material was crushed and the mixture treated with an additional 25 ml. of 48% HF at 100°C for 6 hr., but the product was still inhomogeneous. The product mixture was slurried with 150 ml. H_2O and then filtered. The acidic filtrate (< pH 3) was evaporated as completely as possible in a dry air stream and again gave the large hydrous looking crystals, plus about 3 ml. liquid (40.8 g. total). [The filter cake appeared to be unreacted As_2O_5 (13.5 g. after washing with acetone and vacuum drying). On this basis the theoretical yield of anhydrous $LiAsF_5OH$ would be about 27.1 g. and the 40.8 g. obtained suggests that the $LiAsF_5OH$ contains H_2O or HF solvation (calc. $LiAsF_5OH \cdot 5.5\ H_2O$).]

The small amount of liquid was decanted and the crystals pumped on under vacuum. Portions of the material appeared to be drying to a white solid, but much of the material darkened extensively and the vacuum drying was suspended. Most of the solid dissolved upon the addition of 30 ml. anhydrous ethyl ether, but the resulting brownish solution could not be filtered and all the ether could not be evaporated under the vacuum of the aspirator. The experiment was terminated at this point since the $LiAsF_5OH$ product appeared to have degraded badly. (Similar difficulties in filtration have been experienced in filtering nonaqueous solutions of partially degraded $LiAsF_6$ samples: the properties of the solutions suggest the presence of polymers of the known type, $nM^+(-AsF_4O^-)_n$.)

Second run: Lithium fluoride (13.4 g., 0.518 mole), As_2O_5 (59.3 g., 0.258 mole) and 150 ml. of 48% HF ($\sim$ 4.15 moles) were mixed and heated overnight at $\sim$ 50°C. An additional 50 ml. of 48% HF were then added and the mixture heated on the steam bath 6 hr. The reaction product, consisting of solid lumps in a white slurry, was treated with 200 ml. of 10% HF and then filtered. (The slightly tacky filter cake was only partially

dried after about 60 hr. at 50°C under the aspirator and was not further analyzed.) The filtrate was pumped on at 40°C with a vacuum pump for 35 hr. (About 200 ml. liquid was pumped off.) A white solid separated which was recovered by filtration and dried in a stream of dry air to a final weight of 7.7 g. (Product I-57-B). Elemental analysis gave 11.00% Li; 18.80% As; 36.29% F (total: 65.1%).

The appearance of this material, its low solubility in water and the atomic ratio $Li_{1.00}As_{0.16}F_{1.20}$ suggest that it is much the same composition as Product I-61-C obtained from the LiH_2AsO_4 route. The filtrate was pumped on at 40°C under the aspirator for an additional 60 hr. The liquid, which had darkened slightly (now 125 g.), was cooled to 6°C and then -12°C but very little solid precipitated. Finally, the liquid was cooled to -80°C whereupon much of the liquid solidified. The remaining liquid (16.3 g.) was decanted, but the residual solid remelted on warming. The freezing (-80°C) process was repeated and an additional 3 ml. liquid decanted, but again most of the solid remelted on warming above about -20°C. The slightly yellowish liquid (100 g. after filtration of the small amount of solid) was then heated on a steam bath for 16 hr., whereupon it produced a dark syrupy liquid. Similar darkening occurred when the portions of decanted liquid (i.e., from the freezing step above) were heated on the steam bath. Both liquids were therefore recombined, a few milliliters of 10% HF added and then pumped on under vacuum for two days. The final liquid product (38.8 g.) formed a glass when cooled to -80°C and remelted at about -20°C. Further efforts to isolate a solid product were terminated.

Conclusions: Efforts to prepare ahnydrous $LiAsF_5OH$ have not been successful. The results to date indicate that $LiAsF_5OH$ (like $LiPF_6$) is considerably less stable than $KAsF_5OH$ (which was prepared by one of the two routes studied here) and that the products obtained are largely mixtures of by-products such as LiF, LiH_2AsO_4 and possibly other materials such as the polymeric arsenic-oxy-fluoro species reported to form in the dehydrofluorination of $KAsF_5OH$. Substitution of anhydrous HF for the 48% HF in either variation of this reaction method could probably be used to convert the reactants directly to $LiAsF_6$, but more than one HF step would likely be required and the method does not appear to be competitive with the acid neutralization method.

5. Evaluation of Methods

The desired product, $LiAsF_6$, was successfully prepared by three of the four methods studied, but the first method, neutralization of $HAsF_6$ with LiOH, was far superior. The commercial, crude $HAsF_6$ can be used directly and the $LiAsF_6$ can be separated from the by-products and impurities by solubility methods. The ion exchange method and the AsF_5 method are less well suited experimentally to scale up and both gave products which required purification by solubility methods.

The acid neutralization method was therefore the synthesis method of choice, and recovery and purification procedures were of dominant importance. The key steps in these procedures were indicated to be: (1) neutralization and then removal of the bulk insoluble by-product; (2) heating and concentrating the $LiAsF_6$ to hydrolyze unidentified unstable fluoroarsenate species. (This hydrolysis causes a pH drift to the acidic side which must be corrected: the final solution must be pH stable.) (3) adjustment of pH to about 8 and cooling the solution to minimize the solubility of the lithium arsenates before filtering off the minor insoluble by-products; (4) recovery of $LiAsF_6 \cdot 3H_2O$ by slight further concentration and chilling; (5) recrystallization of the $LiAsF_6 \cdot 3H_2O$ until the desired purity is reached; and (6) vacuum drying of the $LiAsF_6 \cdot 3H_2O$ to anhydrous $LiAsF_6$.

The recrystallization can be performed in water, although the very high solubility of the $LiAsF_6$ requires that several concentration crystallization steps be used to obtain reasonable yields. The use of aqueous isopropyl alcohol for recrystallization of $LiAsF_6 \cdot 3H_2O$ did not appear to offer significant advantages over water alone. Alternatively, the crude $LiAsF_6 \cdot 3H_2O$ could be dried and the anhydrous salt then recrystallized from anhydrous isopropyl alcohol or anhydrous ethyl ether, but these procedures appeared to be inferior to recrystallization from water.

The analytical results for $LiAsF_6$ samples showed that the only significant problems as impurities were oxygenated and carbon-containing species. Unfortunately, these two impurity elements were the most difficult to determine, at the 100 ppm level, in a salt of this type. Overall, however, a combination of analytical methods was developed which appeared to be reliable for analysis of the final product.

IV. PREPARATION OF 2,000 g. OF HIGH PURITY $LiAsF_6$ BY THE ACID NEUTRALIZATION METHOD

The $LiAsF_6$ was prepared by neutralization of hexafluoroarsenic acid with lithium hydroxide:

$$HAsF_6\ (aq.) + LiOH\ (aq.) \longrightarrow LiAsF_6\ (aq.)$$

Reagents: Portions of three different lots of $HAsF_6$ (all from Ozark Mahoning Company) were used in the scale-up preparation of $LiAsF_6$. The $LiAsF_6$ prepared from different lots of acid was combined for convenience of operation and in order to produce a single lot of product for analysis. The major source consisted of $\sim$ 3,950 g. of $HAsF_6 \cdot 6H_2O$ crystals (Lot No. R-4-90).

These which had a wet and slightly dirty greenish appearance and had been used to prepare products I-66-A and III-20-A. A second source consisted of 720 g. of $HAsF_6 \cdot 6H_2O$ crystals (Lot No. R-4-20), which were mostly very white, large crystals. The third source consisted of about 1 liter of green 65% $HAsF_6$ solution, Lot No. BD-1-20, which had been used in our earliest preparations of $LiAsF_6$. Finally nearly 1 liter of rather dark green $HAsF_6$ solution (obtained by combining the "bottom-of-the-bottle" portions of the two lots of crystals with portions of the 65% solution used in our earlier studies of the recrystallization of $HAsF_6$) was filtered before neutralization.

LiOH was obtained as the reagent grade crystals, $LiOH \cdot H_2O$, from Matheson, Coleman and Bell. An ~ 5 M solution of LiOH (i.e., saturated) was prepared and let stand in polyethylene bottles for at least two days and then filtered to remove Li_2CO_3.

Neutralization: About 8,000 g. of acid crystals and solution were neutralized in six batches. The $HAsF_6 \cdot 6H_2O$ crystals were placed in a 4-liter polyethylene beaker and about 16 ml. water per 100 g. acid crystals was added to make a solution. The LiOH solution was added slowly from a polyethylene dropping funnel to the stirred acid solution until the pH reached 7.5-9. The neutralized mixture was then placed in a polyethylene bottle and heated on a steam bath for several hours or overnight to assure that any hydrolytic reactions, such as the hydrolysis of $LiAsF_5OH$, were as complete as possible and filtered (Whatman No. 40 paper) to remove the insoluble by-product, leaving a solution of crude $LiAsF_6$.

The Lot R-4-90 $HAsF_6 \cdot 6H_2O$ crystals ($\sim 3,950$ g.) were neutralized in three approximately equal batches with a total of 5,767 ml. (28.8 moles) of LiOH solution. Each batch was heated overnight, cooled to 5-25°C and filtered. A total of 1,090 g. (wet basis) of insoluble product (of slightly blue-green tint) was removed. The filtrates were concentrated on the flash evaporator at 50-60°C and 30-40 mm. Hg, with a 0° condensing bath. A total of 5,535 ml. water was distilled off. Each batch was adjusted to pH 7-8 and refiltered to remove the insolubles which developed (0.05-0.1 g/100 g. acid crystals), and the concentrates were combined. We observed at this point that the concentrates had a faintly yellowish tinge, which we had not observed previously on any of the smaller scale runs. This color may have been caused by the larger volume of solution, but could be a result of reactions occurring at the steam bath temperature which had not occurred in previous runs, where the neutralized mixture was not heated over about 55°C. Further purification of the $LiAsF_6$ is described in a later paragraph.

The white (Lot R-4-20) acid crystals were thought to be of higher purity, but were found to require nearly as much excess LiOH for neutralization and gave about the same amount of insoluble by-product as did the less pure appearing crystals. Thus, the 720 g. acid crystals (nominally 2.41 moles) required 1,007 ml. (5.03 moles) LiOH solution. The insoluble by-product (173 g. wet basis) from the white acid crystals, however, was white, whereas that from the other acid sources was greenish in proportion to the starting material. Analysis of this white product (87.3 g. vacuum dried) indicated (Found: 17.00% Li; 66.72% F; 16.28% As, total 100.0%) that it was a mixture of composition $LiF \cdot 0.22\ LiAsF_6$.

The filtrate, i.e., the $LiAsF_6$ solution, was concentrated, but after about 800 ml. water had been removed the solution developed a turbidity and acidity (pH ~ 4) just as the other $HAsF_6$ products had done. The pH was readjusted to 7-8 (5 mmoles LiOH), the solution cooled to 3°C and filtered. Evaporation was resumed, but again a slight haze and acidity developed which necessitated pH readjustment (0.25 mmoles LiOH) and refiltration. Evaporation was continued until a total of 1,078 ml. water had been removed. The solution now crystallized almost entirely upon cooling. Just enough water (about 25 ml.) was added to dissolve the crystals with gentle warming. The solution was again turbid, however, illustrating the difficulty of purifying the $LiAsF_6$. The refiltered solution (clear without any yellow tinge) was added to the concentrates from Lot R-4-90 for recrystallization.

The ~ 1 liter of greenish 65% $HAsF_6$ solution (Lot BD-1-20) required 2,745 ml. (13.0 moles) of LiOH solution for neutralization and gave 730 g. (wet basis) of mint green insoluble by-product. An additional 0.05 mole LiOH was required to readjust the pH after the steam digestion. The filtrate had a slight yellow color which increased in intensity upon concentration in the flash evaporator. After 2,435 ml. of water had been removed, the solution crystallized extensively upon cooling. The yellow color was concentrated in the liquid phase which was decanted, neutralized and held for fractional recrystallization. The crystals were combined directly with the concentrates from Lot R-4-90 and R-4-20.

The slightly < 1 liter of emerald green "residual" $HAsF_6$ acid required 2,740 ml. (13.0 moles) of LiOH solution for neutralization and gave 785 g. (wet basis) of mint green insoluble by-product. The yellowish filtrate was concentrated to about 1 liter volume, the pH readjusted (from 6.4 to about 10) and the solution refiltered. After further concentration the solution was cooled. The $LiAsF_6 \cdot 3H_2O$ crystals contained a substantial amount of occluded yellow mother liquor and were therefore not combined directly with the other crystals, but were purified first as described below.

Purification of $LiAsF_6 \cdot 3H_2O$: The purification of the $LiAsF_6$ required the removal of several impurities, one of which was observable by its yellow color and one of which hydrolyzed slowly to generate acidity and other impurities of low solubility such as LiF and lithium arsenates. Four main steps were involved in the purification: (1) The $LiAsF_6 \cdot 3H_2O$ crystals were treated with 1.5-2 ml. water per 100 g., heated to 65-70°C, i.e., above the melting point, and then allowed to recrystallize slowly. This step helped complete the hydrolysis reactions. (2) The crystals were recovered, redissolved in water at 25°, filtered, reconcentrated at 50-55°C on the flash evaporator, and refiltered while warm through Whatman 42 filter paper to remove the insolubles. (3) The solution was then cooled to 25° and/or 0°C and one or two crops of crystals were recovered in a plastic Buchner funnel with Teflon filter or in a coarse fritted polyethylene funnel. The latter permitted good drainage of the turbid filtrate. (4) Within this framework a multiple fractional recrystallization was performed with reworking of filtrates being required because of the very great solubility of the salt.

Thus, 3,685 g. of crystallized $LiAsF_6 \cdot 3H_2O$ was recovered from the three combined large lots and 3,456 g. of doubly recrystallized product was obtained in all. These were then dissolved in 50 ml. of 10^{-3} M LiOH at 69°C and held at this temperature 2 hr. The solution had re-acidified, however, to pH 6 and was readjusted to pH 8. The fractional crystallization was repeated and 3,154 g. was recovered. This was just redissolved in 525 ml. 7×10^{-4} M LiOH at 25°C and held at 45°C over the weekend. The solution (which had maintained a pH of 8.8, but was still faintly turbid) was recooled and filtered through Whatman 42 paper. Finally 2,838 g. of damp $LiAsF_6 \cdot 3H_2O$ crystals was recovered (Lot I-94-E). (Subsequent weight loss on drying indicated a composition of $LiAsF_6 \cdot 3.6H_2O$.) These were dried and analyzed as described in the next section.

In addition to the 2,838 g. of Lot I-94-E hydrated crystals, five nearly saturated filtrates of varying purity remained from the recrystallization. Two of these (about 200 ml. total) contained all of the yellow colored impurity originally present in the neutralized solution (except for any portions removed as insoluble matter). Two other filtrate fractions (about 200 ml. total) were colorless, but these as well as the yellow solutions deposited some white sediment on standing. The fifth filtrate (220 ml.) was that obtained from the Lot I-94-E crystals and was completely colorless and free of turbidity. These solutions probably contained nearly 700 g. of unrecovered $LiAsF_6$.

Preparation of anhydrous $LiAsF_6$: The Lot I-94-E crystals were placed in a 2-liter plastic jar and dried in the lyophylizer at ambient temperature. After 5 days, however, only 537 ml. of water had been removed and the crystals were a hard mass which could not be broken up easily with a spatula. Drying was, therefore, continued under a heat lamp set to maintain a temperature of 40°C inside the lyophylizer. After an additional 2 days the hard mass could be broken up into lumps and drying was continued for 4 days, with occasional interruptions to mix the contents by thoroughly shaking the jar. At this point, about 707 ml. of water had been removed and the $LiAsF_6$ appeared to be anhydrous. About 2,130 g., Lot I-96-A of product was obtained which represents about a 50% yield based on the weight of acid used.

The contents were mixed thoroughly and 250 g. of Lot I-96-A was removed, pumped on separately overnight in the lyophylizer and then submitted for analysis. While results were awaited, the remainder was returned to the lyophilizer and pumped on an additional 4 days and then placed in the dry box for storage.

Following the satisfactory analysis (next section) the $LiAsF_6$ was sealed in glass ampoules under an atmosphere of argon. This was accomplished as follows. Pyrex ampoules which had a ground glass joint were thoroughly cleaned and dried in a vacuum oven at 120°C and then immediately placed in the dry box. The $LiAsF_6$ was loaded through a long-stem funnel in order to keep it from adhering to the neck of the ampoules. A stopcock with connections was then placed on each ampoule so that it could be attached to a glass high vacuum line. The $LiAsF_6$ was then pumped on for at least 1 hr. at 10^{-5} mm. Hg or less. The line and ampoule were then isolated from the pump and filled with 1 atm. of Ultrapure Argon (Matheson). The stopcock was closed and the ampoule cooled with liquid nitrogen, which reduced the vapor pressure of the argon sufficiently that the neck of the ampoule could be sealed off with the torch.

Analysis of high purity $LiAsF_6$: Two (2 g.) samples of Lot I-96-A were submitted to Bell and Howell for spark source mass spectrometric analysis for all impurities. One sample was placed in a screw cap vial which was sealed with tape, and then enclosed in a larger bottle containing Drierite desiccant. The second sample (I-96-AB) was placed in a small (stopcocked) glass tube, pumped on at the vacuum line for 30 min. and then sealed off under an atmosphere of argon, i.e., under conditions very similar to those to be used for final packaging of the bulk high purity samples. In particular, we wished to verify that the glass seal-off did not liberate a significant amount of water which would be condensed onto the $LiAsF_6$.

One sample of Lot I-96-A was submitted to Schwarzkopf Laboratories for major constituent analysis and also for Na, K, H and C. This sample was submitted at the same time as the Bell and Howell samples but was unfortunately delayed en route by the postal strike in effect in the New York area. Subsequently, a sample was submitted to Galbraith Laboratories for C analysis when high, but erratic levels were found initially by the mass spectrometric method. We also analyzed Lot I-96-A in-house for free fluoride ion and also by differential thermal analysis and pyrolysis mass spectrometry. The results of these analyses are shown in Table XII.

The major constituent analyses on Lot I-96-A were satisfactory, although the Li value was as usual (p. 3) slightly low. No free fluoride was detected indicating that this impurity was probably less than 100 ppm. The spark source mass spectrometric analysis showed that all elements except carbon were below the 100 ppm level and showed remarkably good agreement between the two samples for H and O, indicating that the seal-off procedure did not contaminate the product with moisture. Analyses for B, Na, Al, Ca and Cr were also in excellent agreement. The elements N, Si, S and Cl showed a substantial variation, but were in no case above 61 ppm, and the 80 ppm value for K is anomalous.

The two carbon values, 880 and 440 ppm, were then a source of serious concern, both because of their divergence and because, on an atomic basis, over twice as much carbon was indicated as all other impurity elements combined. Also, the carbon level decreased by one-half in the second sample, while the other impurities either stayed about the same or increased with the exceptions of N and S. Thus, the carbon could not be present in a combined form such as carbonate, although it could be present as a fluorocarbon. The reason, as suggested on p. 4), appears to be the reaction of fluorine atoms or molecules during sparking with trace carbon or carbonaceous residues in the instrument. At our request, Bell and Howell kindly re-analyzed Lot I-96-AB for carbon. A new electrode was prepared and analyzed by successive sparkings. As indicated in Table XI, the carbon level decreased rapidly at first and then leveled out slowly, 160 ppm being the result of the fourth analysis.

The carbon analyses by the carbon-hydrogen train method gave slightly lower values, i.e., 0.01% and 0.00% (Schwarzkopf) and 0.012% (Galbraith). Dr. Schwarzkopf stated that the zero value was definitely below 70-75 ppm. The variability of the results may indicate a slight inhomogeneity. The synthesis was not performed in a laboratory having filtered air and contact with suspended particulates was a possibility. Overall, however, the analytical results indicate a level of probably not over 100 ppm carbon.

TABLE XII

ANALYSIS OF HIGH PURITY $LiAsF_6$ (MRI, Lot I-96-A)

Schwarzkopf							Galbraith
Major Constituents (%)			Impurities (ppm)				
Li	As	F	Na	K	H	C	C
3.37	37.95	58.31	ND (< 2)	4	1,500	ND (< 70)	120
3.42	38.11	58.01	ND (< 2)	4	700	100	
Avg. 3.40	38.03	58.16	ND (< 2)	4	1,100	≤ 85	
Li + As + F		99.59	Total, all elements: 99.71%				
Li/As/F	0.965/1.00/6.01		Total, incl. oxygen as 8xH: 100.57%				

SPARK SOURCE MASS SPECTROMETRIC ANALYSIS (Bell and Howell)

	I-96-A		I-96-AB		I-96-AB Carbon Re-analyses (ppm)				
Element	(ppm)	(ppma)*	(ppm)	(ppma)	Order	1	2	3	4
H	16	(392)	11	(270)	16 kv	490		180	
B	ND	-	4.3	(10)					
C	880	(1,795)	440	(900)	24 kv		180		160
N	46	(80)	21	(37)					
O	65	(100)	65	(100)					
Na	28	(30)	28	(30)					
Al	3.3	(3)	5.0	(5)					
Si	13	(11)	70	(61)					
S	43	(33)	ND	-					
Cl	30	(21)	61	(42)					
K	4	(2)	80	(50)					
Ca	15	(9)	15	(9)					
Cr	16	(8)	21	(10)					
Ni	6.7	(3)	24						
m/e = 85	5	(1)	28	(5)					
Total	1,171	(2,486)	873	(1,429)					

* ppma (parts per million atomic) = $\frac{\text{ppm} \times \text{average atomic weight of substance}}{\text{atomic weight ele}}$

The two hydrogen analyses by Schwarzkopf were very high and varied greatly (700 ppm and 1,500 ppm) compared to the spark source results (16 and 11 ppm). As noted previously, this sample was delayed on route and it may have picked up moisture. The large H/As ratio (0.22/1.00) would, however, indicate a composition of $LiAsF_6 \cdot 0 \cdot 11H_2O$. Allowance for the oxygen content leads to a total of well over 100% as shown in Table XII. Alternatively, interferences may affect the combustion method for H analysis on high purity $LiAsF_6$ (for example, if AsF_5 is liberated and reacts with the combustion tube components or water absorbent). Low hydrogen levels had, however, been found previously in $LiAsF_6$ samples of lower purity. Finally, the sample submitted to Swarzkopf may have been inhomogeneous with respect to particles containing some water of hydration. The bulk $LiAsF_6$ samples were, however, dried even further than was the analytical sample in the lyophylizer and also under high vacuum, so that even traces of monohydrate should have been dried. Differential thermal analysis on Lot I-96-A showed absolutely no indication of the presence of $LiAsF_6 \cdot H_2O$. These considerations, together with the observed extremely low H and 0 levels found by spark source lead us to conclude that the $LiAsF_6$ samples as sealed in glass do not contain over 100 ppm H.

V. PROPERTIES OF $HAsF_6$, $LiAsF_6$ AND LITHIUM ARSENATES

Properties of $HAsF_6$: The $HAsF_6$ was obtained from Ozark-Mahoning Company in two forms: as a greenish aqueous solution stated to contain about 65% $HAsF_6$ and 1-3% HF, and as solid crystals stated to be the hexahydrate $HAsF_6 \cdot 6H_2O$ (theoretically 63.8% $HAsF_6$). In either case, neutralization of the acid required over twice as much LiOH as expected based on the nominal $HAsF_6$ content. The crystals required 2.1 times as much and the solution required 2.3 times as much after correction for HF content. A by-product of low solubility was formed during neutralization. Yield of dried by-product is about 0.15 g/g acid crystals, 0.2 g/g acid solution, and 0.1 g/g recrystallized acid. The amounts of excess base required and by-product formed are reduced by recrystallization of the acid, but are not eliminated even by double recrystallization. Furthermore, the neutralized solutions invariably regenerated small amounts of acid values. These effects suggested the presence of one or more inpurities in the $HAsF_6$. These were suspected to be the acid $HAsF_5OH$ and possibly $HAsF_4(OH)_2$, or acid with anions of the form $(\text{-}AsF_4O\text{-})_3^{-3}$ and $(\text{-}AsF_4O\text{-})_n^{-n}$.

Infrared and ^{19}F NMR spectra were obtained on $KAsF_6$, the stock 65% $HAsF_6$ and on recrystallized $HAsF_6$ fractions. The $KAsF_6$ gives an infrared spectrum (KBr pellet) showing strong bands at 703 cm^{-1} (As-F stretch) and 410-390 db. (bending). Not more than a trace of moisture was detected. The ^{19}F NMR spectrum of 1 M $KAsF_6$ was the expected[25] quartet at $\emptyset$ = 64.7 ppm (vs. external $CFCl_3$), J = 933 cps. The stock 65% $HAsF_6$ solution

(between AgCl windows) gives a complex infrared spectrum (from the water, the AsF_6^- bands and unidentified bands), and an NMR spectrum which shows a fluorine-containing impurity in addition to the AsF_6^- quartet. The impurity is removed by recrystallization and is concentrated in the mother liquor. Although the chemical shift of this impurity is approximately the same as that of a fluorine atom bonded to arsenic, it does not have the quartet spectrum required for an As-F coupling, nor does it have the shift expected of free fluoride ion: 129 ppm. However, it could well be a As-F species which is undergoing fast fluoride-exchange reactions in solution, a rather common phenomenon in inorganic fluorides, which would cause collapse of the As-F coupling quartet to a broad band or even a singlet. The recrystallized $HAsF_6$, on the other hand, clearly shows the presence of the AsF_6^- ion by NMR and infrared, i.e., the formula of the acid might be better written as $H_3O^+ AsF_6^- \cdot xH_2O$ where x is probably 4 or 5. The NMR of the recrystallized acid showed only a very small amount of the unidentified impurity. The results of the NMR and IR studies are summarized in Table XIII and in Figure 1.

TABLE XIII

INFRARED AND NMR SPECTRA OF AsF_6^- SALTS AND $HAsF_6$

Compound	Infrared (cm^{-1})[a]	^{19}F NMR (ppm vs. $CFCl_3$)[a]	Assignment
$KAsF_6$	703, 410-390 db.	64.7 (quartet)	AsF_6^-
$HAsF_6$ (stock)	708, 395	64.3 (quartet)	AsF_6^-
	3624, 3500-2600		H_2O
	2000-1700, 1630		
	1200 (v. br.)		Unidentified
		55.7 (singlet)	Unidentified
		40-90 (w. br.)	Unidentified
$HAsF_6$ (recrystallized)	About same as stock, except possibly more abs. in 500-600 region	65.2 (quartet)	AsF_6^-
$HAsF_6$ (green mother liquor)	About same as stock, except possibly 1200 band sl. more intense	57.7 (singlet)	Unidentified
		40-90 (w. br.)	Unidentified
		65 (v. wk. quartet)	AsF_6^-

[a] Infrared spectra obtained on a Beckman IR-12; NMR spectra obtained on a Varian HA-100 Spectrometer. The $HAsF_6$ solutions were contained in Teflon inserts because of the HF.

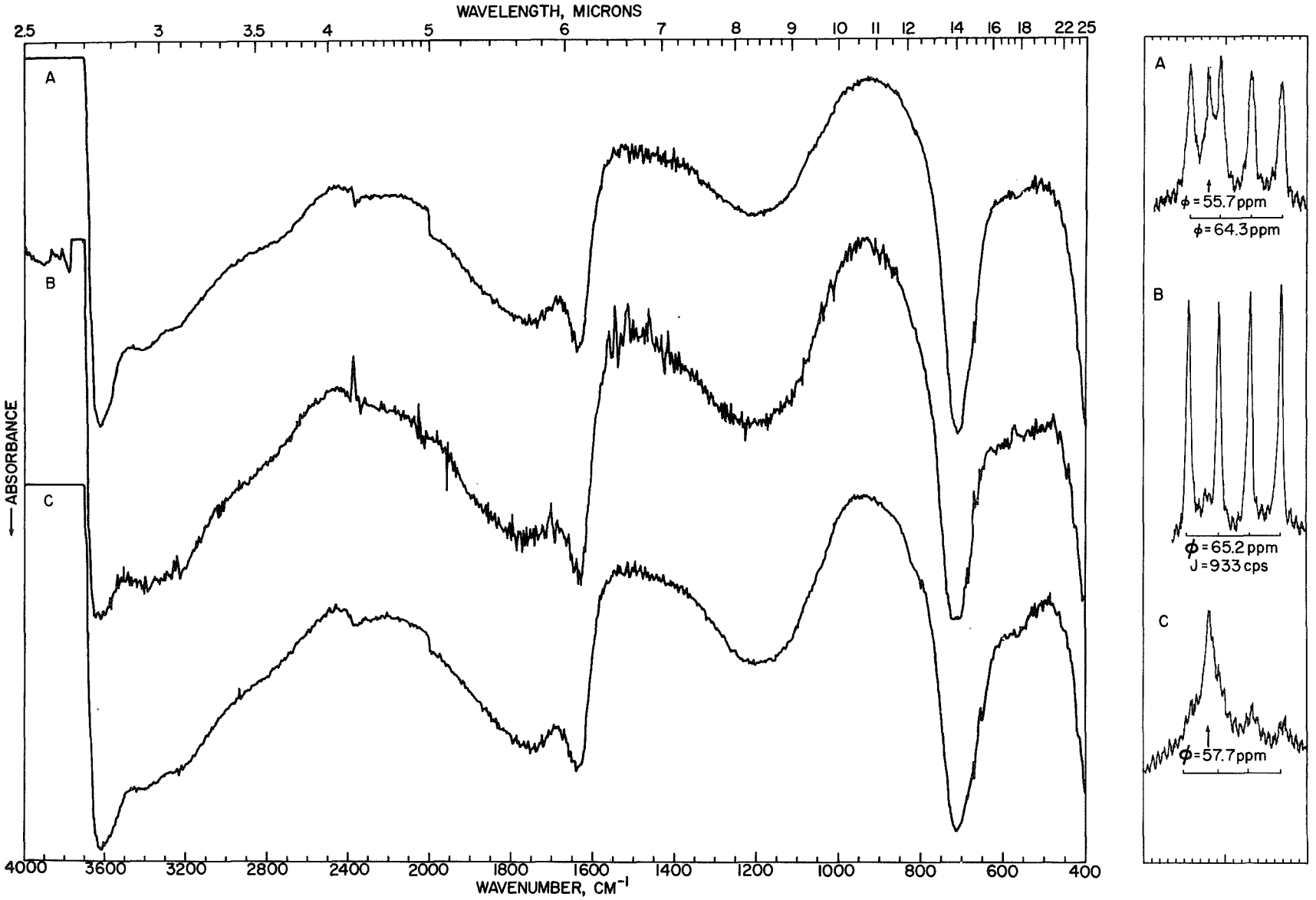

Figure 1 - Infrared and NMR Spectra of $HAsF_6$ Fractions
Sample A is Stock 65% $HAsF_6$ Solution (greenish)
Sample B is Twice Recrystallized $HAsF_6$ (faint green)
Sample C is Mother Liquor from Recrystallization (dark green)

On the basis of these results and the hydrolysis behavior, we conclude that the $HAsF_6$ has at least three impurities, in addition to the HF. The major impurity is characterized by rapid hydrolysis in neutral solution and may be the species giving the ^{19}F singlet at 55.7 ppm. A second impurity is characterized by slow hydrolysis in neutralized solution. Both of these appear to be fluoroarsenate species. The third impurity is minor, but is responsible for the green color in 65% $HAsF_6$ and possibly for the yellow color observed during workup of the large scale run of $LiAsF_6$. Fortunately, all of these impurities can be removed during $LiAsF_6$ preparation.

The $HAsF_6 \cdot 6H_2O$ crystals dissolve endothermically in H_2O and a batch prepared by recrystallization of the 65% solution turned to a black oil upon drying in vacuo at ambient temperature.

Properties of $LiAsF_6$: Anhydrous lithium hexafluoroarsenate is a stable white solid. A sample sealed under dry air in a melting point tube gave evidence of dissociation and attack on the glass at about 350°C, but some $LiAsF_6$ remained after recooling from a maximum temperature of 370°C. Differential thermal analysis* of the pure salt shows only an endotherm (Figure 2A) at 258°C. This endotherm appears to be a crystal transition rather than a melting point. A sample was also subjected to pyrolysis mass spectrometry.** The ion current was monitored continuously and complete mass spectra were recorded at 22, 90, 150, 250, 280, 340, and 380°C. The onset of decomposition, as indicated by the increasing ion current (Figure 2B) was at about 280°C. The evolution of AsF_5 was observed by the mass spectra, i.e., by the ions AsF_4^+, AsF_2^+ etc. The ions AsF_3O^+ and HF^+ were also observed, probably a result of the reaction of AsF_5 with impurities in the instrument. Other minor impurities such as Na^+ and SiF_3^+ were observed also, but all the major peaks were As-F species. Rather surprisingly, a peak at mass 300 attributable to As_4^+ was observed at 340° and 380°C indicating a complete loss of fluorine from the arsenic.

The $LiAsF_6$ is hygroscopic, forms at least two hydrates, becomes deliquescent at about 30-35% relative humidity, and is very soluble in water. At room temperature 1 ml. water dissolves about 1.9 g. $LiAsF_6$ with the evolution of considerable heat. The saturated solution has a density of about 1.85 g/cm^3. Hydrous looking crystals of $LiAsF_6 \cdot 3H_2O$ are obtained upon cooling the saturated solution, or upon distilling off the water up to its melting point of 58°C. (Weight loss on the recovered crystals varied from 3.5 to 4 moles water per mole $LiAsF_6$. The hydration number was established by equilibrating $LiAsF_6$ at 20% relative humidity and by DTA.)

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* A Du Pont Model 900 DTA instrument was used with a heating rate of 15°C/min. Exposure of the sample to moisture was avoided.

** An Atlas CH-4B Mass Spectrometer equipped with a direct inlet probe for solids was used. The heating rate was about 40°C/min. (average over the range 100-380°C).

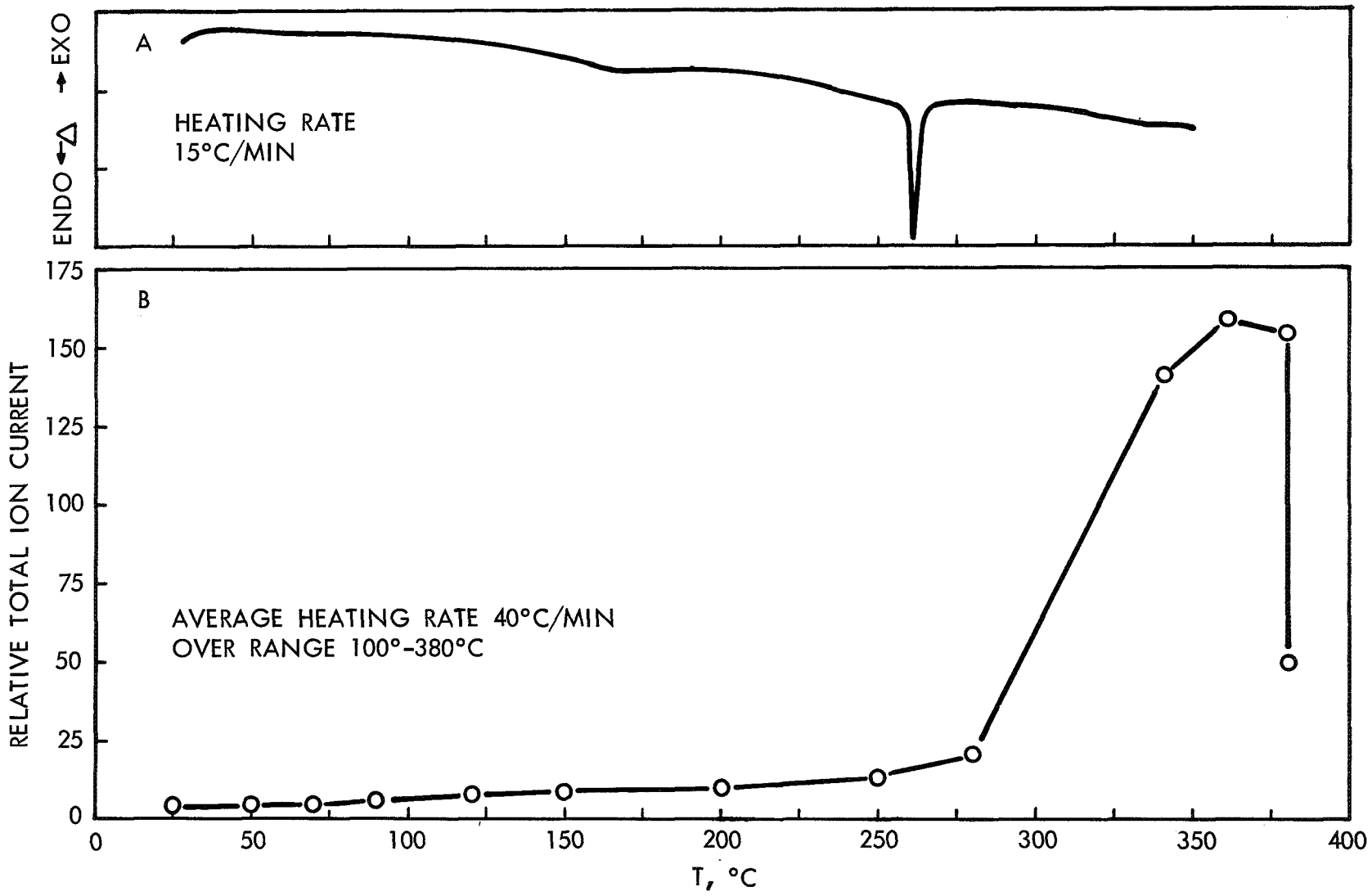

Figure 2 - Thermal Stability of $LiAsF_6$

(A) Differential Thermal Analysis of $LiAsF_6$ (Lot I-96-A)

(B) Pyrolysis Mass Spectrometry of $LiAsF_6$ (Lot I-96-A)

When the trihydrate was dried in a stream of dry air, the powdery monohydrate, melting point 117°C, was formed. This product (apparently also formed when the saturated solution was distilled to dryness at 80°C) is converted to the anhydrous salt by pumping at 0.005 mm. Hg and ambient temperature.

Mixtures of anhydrous $LiAsF_6$ and H_2O in mole ratios of 1 to 6, 1 to 7 and 1 to 8 first solidified at -25°, -27° and -31°C, respectively, but all gave a DTA endotherm at -47°C, which may be the eutectic. The trihydrate dissolves in water endothermically.

The $LiAsF_6$ is soluble in ethyl ether at about 0.55 g/ml and forms a $LiAsF_6 \cdot 2Et_2O$ which is white crystals at 25°C. Another solvate $LiAsF_6 \cdot 6Et_2O$ was observed at -80°C. The $LiAsF_6$ is soluble in isopropyl alcohol at about 0.8 g/ml. A solid solvate was formed at -20°C, but it melted upon warming to room temperature.

The ^{19}F NMR spectrum of a sample of $LiAsF_6 \cdot H_2O$ dissolved in water contained only the AsF_6^- quartet at $\emptyset$ = 64.4 ppm and its ^1H spectrum in $(CD_3)_2CO$ solution contained only a singlet at σ = 3.88 ppm attributable to water.

The infrared of all early $LiAsF_6$ samples contained water bands at 3450 and 1640 cm^{-1}. Some of the samples appear to contain residual H_2O whereas others appeared to be picking up H_2O during the KBr pellet preparation. The KBr-sandwich technique[26] was then employed to exclude absorption of moisture from the air. The spectrum of the anhydrous salt contains only the AsF_6^- bands at 712 cm^{-1} and 410-420 (db) cm^{-1}. The spectra of the hydrated salts varied with the degree of hydration, but the $LiAsF_6 \cdot H_2O$ had the AsF_6^- bands at 708 and 395-411 cm^{-1} and the water bands at 1640 and 3450 cm^{-1}. The presence of the trihydrate appears to contribute to a weak broad absorption in the region of $\sim$ 500 cm^{-1} and to a lesser extent at $\sim$ 850 cm^{-1}.

Properties of lithium arsenates: The neutralization of $HAsF_6$ solutions produces considerable insoluble by-product which appears to be a mixture of lithium fluoride and a lithium arsenate. Some additional small amount of white solid comes out of the $LiAsF_6$ solution during product work-up. Finally, many of the samples of dried $LiAsF_6$ gave a slightly turbid saturated aqueous solution, which together with the oxygen levels found in the impurity analyses suggested that arsenates were primarily responsible. The lithium arsenates are apparently not well characterized: The Handbook of Chemistry and Physics lists only the ortho-arsenate Li_3AsO_4 as an anhydrous white powder of density 3.07 g/cm^3 which is very slightly soluble in cold water, soluble in dilute acid, but insoluble in pyridine.

The mono- or dilithium salts and the meta arsenate are not listed.* The three dissociation constants for arsenic acid are listed as: $K_1 = 5.62 \times 10^{-3}$; $K_2 = 1.70 \times 10^{-7}$; $K_3 = 3.95 \times 10^{-12}$ (at 18°C), i.e., it is just slightly stronger than phosphoric acid. The pH of the $LiAsF_6$ solutions are usually in the range 6-8, sometimes drifting to the acidic side during product work-up. The solubilities of the LiH_2AsO_4 and Li_2HAsO_4 were therefore of sufficient interest that small samples were prepared for examination.

Samples of LiH_2AsO_4, Li_2HAsO_4 and Li_3AsO_4 were prepared by weighing out the stoichiometric amounts of anhydrous LiOH and As_2O_5, adding sufficient water to produce a slurry and then heating 1 hr. at 70°C. The 2:1 and 3:1 reaction mixtures remained as slurries. The solids were filtered off and dried in the lyophylizer, to give white powders. The 1:1 reaction mixture contained much less solid. Most of this was dissolved by additional water, the solution filtered and the solvent evaporated. The paste-like LiH_2AsO_4 was then dried in the lyophylizer to give a white wax-like solid. Elemental analyses (Galbraith Laboratories) are shown below.

	Li	H	As	O (Diff.)	Li/H/As
LiH_2AsO_4, Theoret.	4.67	1.35	50.6	43.3	
Found	4.71	1.35	48.18	45.76	1.00/1.99/0.95
Li_2HAsO_4, Theoret.	9.03	0.65	48.7	41.6	
Found	10.22	0.57	45.36	43.85	2.00/0.77/1.08
Li_3AsO_4, Theoret.	13.01	-	46.9	40.1	
$Li_3AsO_4 \cdot 1/2H_2O$,					
Theoret.	12.36	0.59	44.4	42.8	
Found	12.44	0.48	42.85	44.23	3.00/0.80/1.48

The data are consistent with the presence of some of the trilithium salt in the Li_2HAsO_4 and with much of the trilithium salt being in the form of the hemihydrate. The analogous salt, $Li_3PO_4 \cdot 1/2H_2O$, is known.

Solubility tests showed that LiH_2AsO_4 was by far the most soluble in water: 0.5 g. dissolved completely in 5 ml. whereas this quantity of Li_2HAsO_4 or Li_3AsO_4 did not dissolve noticeably in 10 ml. of H_2O. None of the three salts appeared to dissolve at this level in ethyl ether or isopropyl alcohol. The three salts in water (0.8 g/20 ml) gave mixtures with the following pH.

LiH_2AsO_4	6.5
Li_2HAsO_4	7.6
Li_3AsO_4	11.6

* The LiH_2PO_4, Li_3PO_4 and $LiPO_3$ are listed, the latter two stated to have very low solubilities in water.

VI. DISCUSSION OF RESULTS AND CONCLUSIONS

Methods of preparing and analyzing high purity $LiAsF_6$ have been developed. Four possible synthesis methods were evaluated, three were demonstrated successfully, and one superior method was scaled up to produce over 2,000 g. of high purity product. Analytical methods for major constituents and impurity elements were cross-checked by two or more methods or independent laboratories on standard samples of LiF and As_2O_3 and also on several $LiAsF_6$ samples. The final product was analyzed for all impurities by spark source mass spectrometry. The elements Na and K were cross-checked by atomic absorption spectrophotometry and C and H were cross-checked by combustion train techniques. The final product was also checked by differential thermal analysis and by a concentrated solution turbidity test, as well as by duplicate analyses for Li, As and F.

The final product was prepared by neutralizing commercially obtained 65% $HAsF_6$ solution and $HAsF_6 \cdot 6H_2O$ crystals, and some lower grade solution (remaining from acid recrystallization studies), about 8,000 g. in all, with 5 M LiOH solution. Hydrated $LiAsF_6$ was then recovered by a filtration-concentration-refiltration and crystallization procedure. This product was subjected to multiple fractional recrystallization from water and dried in vacuum to give 2,130 g. of the anhydrous salt. Analysis indicated that it contained not more than 100 ppm of any impurity on an elemental basis. The method could probably be scaled up to the pre-pilot level with only minor modifications.

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APPENDIX

DETECTION LIMITS AND DEVIATION OF ANALYTICAL METHODS FOR IMPURITIES

Spark Source Mass Spectrometry: The Bell and Howell technical brochure states that their standard survey analysis has a nominal detection limit of 0.2 to 1.0 ppma*, and a precision of $\pm$ 20% (being limited by the photographic detection plates**). The detection limit depends to some extent on the element sought and the composition of the sample. In the analyses of samples of LiF, As_2O_3 and $LiAsF_6$ Bell and Howell listed the detection limits shown below for those elements which were detected and state that all other elements are present at less than 5 ppma. These detection limits are listed in Table A-I.

Emission Spectrography: Coors Spectrochemical Laboratories perform emission spectrographic analyses at three levels of authority: (1) semiquantitative analyses in which 35 elements are sought and results are reported as: major (10%), minor (1-10%), low minor (0.1-1%), and trace (< 0.1%); (2) quantitative estimate in which specific elements are analyzed and reported with the deviation of 2/3 to 3/2 of the actual value (i.e., -33% to +50%); and (3) quantitative analysis for specific elements using internal standards, the deviation being $\pm$5-10%. In Chemo-Services' semiquantitative analysis 40 elements are sought (including six, Au, Ga, In, Rh, Pt, and W, not sought by Coors, but omitting one, Tl, sought by the latter). They reported a concentration range for elements detected and an upper limit possible for all others sought. Chemo-Services also supplies quantitative emission analyses, using internal standards for each element requested. The detection limits indicated by Coors for their quantitative estimate and by Chemo-Services for their semiquantitative analyses are summarized in Table A-II.

Atomic Absorption Spectrophotometry: At least 65 metal and metalloid elements are amenable to AA Spectrophotometric analysis, according to the catalogue of Varian-Techtron Pty. Ltd., but each element requires the use of a specific lamp for its analysis. The nominal sensitivity is excellent for nearly all these elements, but the detection limits are said to depend on operating procedures and other factors such as enhancement

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* Detection limits of 0.05-0.3 ppma (parts per million atomic) and 0.01-0.05 ppma are available in special analyses.

** The use of an electronic detection method together with internal standards is claimed to give a precision of $\pm$ 5% and nominal detection limits of 0.05 ppma for specific elements sought.

by use of certain solvents, e.g., methyl ethyl ketone. The sensitivity* as reported by Varian and the detection limits for those elements for which Chemo-Services** and Coors state they have analytical capability are listed in Table A-III (the lanthanides have been grouped together for brevity). The AA method is stated to be much more amenable to quantitative analysis than is emission spectrography, but deviations of routine analyses are probably of the order of $\pm 1\%$.

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* Sensitivity is defined as the concentration of an element in aqueous (in ppm) which is needed to produce 1% absorption.

** Although Chemo-Services state this capability, they could not run the arsenic compounds which we submitted, because of lack of adequate hood ventilation of the burner assembly.

TABLE A-I

DETECTION LIMITS IN SPARK SOURCE MASS SPECTROMETRIC ANALYSIS OF SPECIFIC SAMPLES

Element	Detection Limit (ppma)[a/]		
	LiF	As_2O_3	$LiAsF_6$
H	1	1	7
B	-	-	0.7
C	3	1	0.7
N	3	-	2
O	3	-	0.7
Na	0.7	0.3	0.1
Mg	1	-	0.7
Al	1	-	0.7
Si	3	-	1
P	3	-	-
S	3	-	1
Cl	3	1	1
K	0.7	0.3	0.3
Ca	1	-	1
Ti	-	-	2
Fe	3	-	2
Co	3	-	-
Ni	3	-	2
Cu	3	-	2
Zn	3	-	3
Ga	-	-	1
Ge	-	-	3
Se	-	-	3
In	-	-	1
Sb	-	3	3

a/ Parts per million atomic; $ppm = ppma \times \frac{\text{at. wt. of element}}{\text{ave. at. wt. of substance}}$

TABLE A-II

REPORTED DETECTION LIMITS BY
EMISSION SPECTROGRAPHIC ANALYSIS

Element	Detection Limit (ppm) Chemo-Services Semiquantitative	Coors Quantitative Estimate
Li	500	25
Be	5	1
B	10	1
Na	500	75
Mg	5	1
Al	10	1
Si	10	1
P	1,000	75
K	10,000	10 (if requested)
Ca	100	5
Ti	1	5
V	5	5
Cr	100	5
Mn	5	1
Fe	10	1
Co	10	10
Ni	10	10
Cu	1	1
Zn	100	25
Ga	10	5
Ge	5	1
As	100	25
Sr	100	50
Zr	10	25
Nb (Cb)	100	50
Mo	5	10
Rh	50	-
Ag	1	1
Cd	100	25
In	10	1
Sn	5	5
Sb	50	10
Te	-	25
Ba	100	1
Ta	500	50
W	100	100
Pt	10	-
Au	10	-
Hg	1,000	10
Tl	-	75
Pb	5	1
Bi	5	10

TABLE A-III

REPORTED SENSITIVITY AND DETECTION LIMITS BY ATOMIC ABSORPTION ANALYSIS

Element	Sensitivity (ppm) Varian	Detection Limit (μ g/ml solutions)[a] Chemo-Services	Coors
Li	0.02	0.005	-
Be	0.02	0.002	0.1
B	11	6	-
Na	0.004	0.002	0.01
Mg	0.006	0.0003	0.001
Al	1	0.1	1
Si	2.1	0.1	1
K	0.01	0.005	0.05
Ca	0.03	0.002	0.05
Sc	0.53	0.1	-
Ti	2.2	0.1	-
V	1.2	0.02	1
Cr	0.09	0.005	0.1
Mn	0.04	0.002	0.05
Fe	0.08	0.005	0.1
Co	0.09	0.005	0.1
Ni	0.07	0.005	0.1
Cu	0.04	0.005	0.05
Zn	0.01	0.002	0.01
Ga	1.5	0.07	-
Ge	2	1	-
As	1.3	0.2	1
Se	0.6	0.5	1
Rb	0.04	0.005	1
Sr	0.06	0.01	-
Y	5	0.3	5
Zr	12	5	-
Nb	20	3	-
Mo	0.4	0.03	0.5
Ru	1.3	0.3	-
Rh	0.23	0.03	-
Pd	12	0.02	-
Ag	0.04	0.005	0.001
Cd	0.02	0.005	0.005
In	0.4	0.05	-
Sn	0.4	0.06	1
Sb	0.64	0.1	0.1
Te	0.3	0.3	-
Cs	0.16[b]	0.05	50
Ba	0.32	0.05	2
Lanthanides	0.04-72	0.08-50	10 (Dy)
Hf	14	15	-
Ta	11	5	-
W	5.3	3	10
Re	11	1.5	-
Os	1.3	-	-
Ir	4.1	2	-
Pt	2	0.1	1
Au	0.3	0.02	0.1
Hg	2	0.5	2
Tl	0.3	0.025	-
Pb	0.16	0.03	0.1
Bi	0.22	0.05	-
U	120	30	-

a/ 1 μg/ml = 1 ppm for aqueous solutions.
b/ With special photomultiplier tube.

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Attn: Dr. A. Moos

Honeywell Inc.
Livingston Electronic Laboratory
Route 309
Montgomeryville, Pennsylvania 18936
Attn: Library

Lockheed Missiles & Space Company
P. O. Box 504
Sunnyvale, California
Attn: R. E. Corbett
Dept. 62-14, Bldg. 154

Lockheed Missiles & Space Company
Dept. 62-30
3251 Hanover Street
Palo Alto, California 93404
Attn: J. E. Chilton

Lockheed Missiles & Space Company
Technical Information Center
3251 Hanover Street
Palo Alto, California 93404

P. R. Mallory & Co., Inc.
Northwest Industrial Park
Burlington, Massachusetts 01803
Attn: Dr. Per Bro

P. R. Mallory & Company, Inc.
Technical Services Laboratory
Indianapolis, Indiana 46206
Attn: A. S. Doty

P. R. Mallory & Co., Inc.
3029 E. Washington Street
Indianapolis, Indiana 46206
Attn: Technical Librarian

Marquardt Corporation
16555 Saticoy Street
Van Nuys, California 91406
Attn: Dr. H. G. Krull

Martin Company
Electronics Research Department
P. O. Box 179
Denver, Colorado 80201
Attn: William B. Collins, MS 1620
M. S. Imanura, MS 8840

Material Research Corporation
Orangeburg, New York 10962
Attn: V. E. Adler

Mauchly Systems, Inc.
Montgomeryville Industrial Park
Pennsylvania 18936
Attn: John H. Waite

Melpar
Technical Information Center
7700 Arlington Boulevard
Falls Church, Virginia 22046

McDonnell Douglas Corp.
3000 Ocean Park Blvd.
Santa Monica, California 90406
Attn: A. D. Tonelli, MS-7C

North American Rockwell
Autonetics Division
P. O. Box 4181
Anaheim, California 92803
Attn: R. F. Fogle, GFIG

Metals and Controls Division
Texas Instruments, Inc.
34 Forrest Street
Attleboro, Massachusetts 02703
Attn: Dr. E. M. Jost/Dr. J. W. Ross

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110
Attn: Physical Science Laboratory

North American Aviation, Inc.
12214 Lakewood Boulevard
Downey, California 90241
Attn: Burton M. Otzinger

North American Aviation, Inc.
Rocketdyne Division
6633 Canoga Avenue
Canoga Park, California 91303
Attn: Library

North American Aviation Co.
S&ID Division
Downey, California 90241
Attn: Dr. James Nash

Ozark-Mahoning Company
310 West 6th Street
Tulsa, Oklahoma 74119
Attn: Dr. Wayne E. White

Oklahoma State University
Stillwater, Oklahoma 74075
Attn: Prof. William L. Hughes
School of Electrical Engineering

Dr. John Owen
P. O. Box 87
Bloomfield, New Jersey 07003

Power Information Center
University City Science Institute
3401 Market St., Rm. 2107
Philadelphia, Pennsylvania 19104

Prime Battery Corporation
15600 Cornet Street
Santa Fe Springs, California 90670
Attn: David Roller

Portable Power Sources Corp.
122 East 42nd Street
New York, New York 10017
Attn: L. Schulman

RAI Research Corporation
36-40 37th Street
Long Island City, New York 11101

Philco Corporation
Division of the Ford Motor Company
Blue Bell, Pennsylvania 19422
Attn: Dr. Phillip Colet

Radio Corporation of America
Astro Corporation
P. O. Box 800
Hightstown, New Jersey 08540
Attn: Seymour Winkler

Philco-Ford Corporation
Space Power & Prop. Dept. MS W-49
3825 Fabian Way
Palo Alto, California 94303
Attn: Mr. D. C. Briggs

Radio Corporation of America
415 South Fifth Street
Harrison, New Jersey 07029
Attn: Dr. G. S. Lozier
Bldg. 18-2

Southwest Research Institute
8500 Culebra Road
San Antonio, Texas 78206
Attn: Library

Sonotone Corporation
Saw Mill River Road
Elmsford, New York 10523
Attn: A. Mundel

Thomas A. Edison Research Laboratory
McGraw Edison Company
Watchung Avenue
West Orange, New Jersey 07052
Attn: Dr. P. F. Greiger

Texas Instruments, Inc.
P. O. Box 5936
Dallas, Texas 75222
Attn: Dr. Isaac Trachtenberg

Stanford Research Institute
820 Mission Street
South Pasadena, California 91030
Attn: Dr. F. R. Kalhammer

TRW Systems Inc.
One Space Park
Redondo Beach, California 90278
Attn: Dr. A. Krausz,
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TRW Systems, Inc.
One Space Park
Redondo Beach, California 90278
Attn: Dr. Herbert P. Silverman (R-1/2094)

TRW, Inc.
2355 Euclid Avenue
Cleveland, Ohio 44117
Attn: Librarian

Tyco Laboratories, Inc.
Bear Hill
Hickory Drive
Waltham, Massachusetts 02154
Attn: Dr. A. C. Makrides

Unified Sciences Associates, Inc.
2925 E. Foothill Blvd.
Pasadena, California 91107
Attn: Dr. S. Naiditch

Union Carbide Corporation
Development Laboratory Library
P. O. Box 6056
Cleveland, Ohio 44101

Union Carbide Corporation
Parma Laboratory
P. O. Box 6116
Parma, Ohio 44130
Attn: Dr. Robert Powers

University of California
Space Science Laboratory
Berkeley, California 94720
Attn: Dr. C. W. Tobias

University of Pennsylvania
Electrochemistry Laboratory
Philadelphia, Pennsylvania 19104
Attn: Prof. John O. M. Bockris

University of Toledo
Toledo, Ohio 43606
Attn: Dr. Albertine Krohn

Westinghouse Electric Corporation
Research and Development Center
Churchill Borough
Pittsburgh, Pennsylvania 15235
Attn: Dr. C. C. Hein/Dr. A. Langer

Yardney Electric Corporation
40 Leonard Street
New York, New York 10013
Attn: Dr. George Dalin

Western Electric Company
Suite 802, RCA Building
Washington, D. C. 20006
Attn: R. T. Fiske