The Design of a Heated Mass Spectrometer Ion Source for Isotope Abundance Measurements.

by

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ABSTRACT

A simple furnace type mass spectrometer positive ion source has been designed constructed and tested. This source operated satisfactorily under certain conditions and was used in the determination of the relative abundances of the copper isotopes.

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INTRODUCTION

Positive ion sources designed for mass spectrometer or mass spectrograph enalyses of solids, non volatile at ordinary temperatures, have been reported in the scientific literatures, (1)...(37). Each of these is one of the three distinct types:

(a) Furnace Source, (b) Heated Filament Source or (c) Spark Source.

Furnace Source.

The furnace source employs a small electrically heated vapourizing chamber or "furnace", containing the sample to be vapourized and mounted in such a manner that the emergent vapours pass into the ionizing chamber of the source. Ionization is brought about by bombardment with electrons of specific energy. The furnace, if constructed of metal, may carry the heating current, thus acting as both heating element and vapourizing chamber. Otherwise, the furnace is heated by an electrically insulated heating element, (1)...(16).

In order to produce positive ion currents of the order of 10^{-13} amperes the furnace must maintain a steady pressure of about 10^{-1} mm., due to the sample in the ionization chamber, (4),(14). This means it must operate satisfactorily at a temperature corresponding to a sample vapour pressure of approximately 10^{-3} mm. The substance from which the furnace is constructed places a maximum on its satisfactory operating temperature. Nier found this limit to be 1200° C. for Nichrome V, (4), while Bleakney and Sampson found it to be 2500° C. for tungsten, (5). However, samples have been analysed using this type of source at temperatures ranging from 38° C. to 2000° C. (Table 1).

Well resolved and steady ion currents are not readily obtained from samples which are hygroscopic. For best results such samples should be handled entirely in a dessicated atmosphere. A small furnece could be loaded under these conditions, but would necessarily be exposed to the atmosphere during the process of its being mounted in the mass spectrometer tube. White and Cameron state that if possible the sample in question should be studied in an element or compound form which is not hygroscopic, (1). Nier has obtained relative abundance measurements for normal uranium from samples of UClh and UBrh, both of which are quite hygroscopic, (16). Random fluctuations in ion currents resulted in an isotope abundance ratio with 1.0% precision, although twenty-six separate measurements were made.

There is the possibility of preferential isotope evaporation when a furnace type source is used. Vapourization is a surface effect and when it takes place from the liquid state the lighter isotope (Mass M_1) is favoured in the vapour phase by a factor $(M_2/M_1)^{\frac{1}{2}}$. Until such time as a steady state is reached, vapourization takes place at a greater rate than mixing within the sample. There is, therefore, an isotope effect which gives rise to mass discrimination. If such an effect exists isotope abundance ratios are found to change with time of heating.

Nier investigated the abundance ratios for calcium in this respect, (4). He vapourized the calcium from the solid state and as would be expected, he found no change of the calcium isotope abundance ratios with time of heating. There is no appreciable mixing in the solid state and hence no change in the ratios with time.

For heavier ions this effect is less pronounced because with increase in atomic number there is a marked decrease in the factor $(M_2/M_1)^{\frac{1}{2}}$.

The furnace type source produces singly and multiply charged positive ions. This is an important factor in abundance ratio work. The presence of multiply charged ions permits the checking of relative abundances by the study of several different sets of ions for each sample analysed. With multiply charged ions, it is possible in general to make relative abundance measurements in a mass range free of residual ions.

Table 1 shows the solid samples which have been studied with mass spectrometers using furnace type positive ion sources. In all, thirty-three elements ranging in mass numbers from 7 to 238 have been vapourized from the liquid state or the solid state. Hygroscopic samples, samples which sublime and samples which decompose have been analysed successfully. The range of temperatures covered is from less than 200°C. to greater than 2000°C. Singly and multiply charged ions have been produced, although the latter have not been considered in every case. If obtainable in a suitable element or compound form having an appreciable vapour pressure at a temperature below 2000°C., any solid sample non volatile at ordinary temperatures may be analysed through the use of a furnace type positive ion source.

Filament Source.

The filament source employs a metal filament which may be a disc, tube, strip or helix, coated or impregnated with the sample. The passage of an electric current through this filament causes the

thermionic emission of positive ions, (17)...(27).

metal in vacuum be possible, the electron work function of the surface of the filament must exceed the ionization potential of the metallic sample with which the filament is coated or impregnated. The mechanism of thermionic emission is essentially the same as that of the formation of ions from vapour. In the case of thermionic emission the atoms to be ionized reach the surface by diffusion from within, a process which is enhanced by the heat of the filament. For positive ion emissions which are sufficiently steady to give reproducible values over a range of temperature the Richardson equation:

is found to hold. I is the saturation current per square centimeter of emitting surface. A is a universal constant, T is the absolute temperature and b depends upon the nature of the metal and the temperature. In general, positive thermions will be emitted from such samples if they are heated on suitable filaments to temperatures just less than their respective melting points, (38).

The lighter of two isotopes in a heated sample has the greater thermal velocity. Thermionic emission is a surface effect and if it proceeds from the liquid state, in which there is perfect mixing at the surface, the lighter isotope (mass M_1) is favoured in the vapour state by a factor $(M_2/M_1)^{\frac{1}{2}}$. If, however, the thermionic emission proceeds from the solid state, where there is no such mixing, this isotope effect is not detected, (21),(27). When a filement source

is used as a source of positive ions in mass spectrometer relative abundance studies, such an isotope effect would lead to mass discrimination.

Positive thermions are readily obtained from many salts.

Most common salts emit positive ions when heated to about 700°C. The more electro-positive the metallic constituent of the salt the greater is the ion emission. The most mobile ion of the salt is found to be the one emitted, (38),(19). In the case of the lead halides only the negative halide ions are detected. Cd and Zn ions are emitted from CdI₂ and ZnCl₂. Investigations show that the positive ions emitted correspond in general to those formed during electrolysis of the salts. These are, in the case of CdI₂ and ZnCl₂, Cd and Zn . It is also known that, in thermionic emission from alkali metal salts, singly charged alkali ions attached to molecules of the salt are formed. That is to say, ionic and molecular evaporation proceed simultaneously, (38).

Ternary systems prove to be better thermionic emittors than do binary ones (17). This is because the ternary system is in all probability a three dimensional network of three different types of ions, - one of which floats in the "holes" characteristic of such networks. Therein, it is free to migrate to the surface and be emitted under the influence of a small potential. It has been established that such is the structure of the alkali aluminium silicates which have proven to be excellent emittors of alkali as well as aluminium positive thermions.

A good emittor should have an ionic lattice with the ions being held in the lattice by small forces only (17). Otherwise, the

compound should be thermally stable in order that available energy can be concentrated to break down the ionic lattice. If there is an absence of lattice structure of any kind, as is the case with metals, ideal vapourization may be realized.

Table (2) shows the samples which have been studied mass spectrometrically, using filament type sources. The elements in - vestigated are mainly alkalies or alkaline earths. All of these elements with the exception of Al, Ce, Y, and V have been studied through the use of furnace type sources. A serious disadvantage of the thermionic emission or filament source is the absence of multiply charged ions in the majority of cases (17).

Spark Source.

The spark sources reported in the scientific literature are of two kinds. First, there is the Dempster Spark Source (29). In this positive ion source a high frequency oscillating spark is in - ductively coupled to two electrodes one or both of which may be the element or a compound of the element to be investigated. This nature of source is powerful. It will produce ions with platinum and gold, elements which are ionized with great difficulty by any means. Singly and multiply charged ions are produced. Secondly there is the discharge tube containing an inert gas. A high voltage discharge gives rise to positive ions of the cathode material or of the sample placed in the well of the cathode. The inert gas helps maintain the discharge across the tube. This source has been used effectively in spectroscopy for a number of years. It too is quite efficient (28)...(37).

Table (3) shows the elements which have been studied with mass spectrographs using one or other of these types of sources. This nature of source does not lend itself favourably to mass spectrometer work.

It produces multiply charged ions which, enroute to the focuseing field, may change their charges, thus giving rise to spurious ion currents. Also there is the problem of shielding the ion current collector as well as the extremely sensitive D.C. ion current amplifier from the effects of the fluctuating fields set up by either of these ion sources. Finally a spark type source does not give rise to an ion current of constant magnitude. This is not serious in isotope detection work as done with mass spectrometers and spectrographs but it does make precision relative abundance measurements impossible.

experimental

Apparatus

The mass spectrometer used is of a 90° sector type (39).

Figure 2, (c) and (d) shows the small electrically heated furnace in detail. The 0.040° nickel sleeve, when loaded with a sample, is closed at each end with a nickel plug. A small hole is pricked at the centre of the loaded sleeve which is then spot welded to the lower terminals of the two small press seals held in place on the lid of the furnace with a spring clamp and screw (Fig. 2,d). Care is taken to have the hole in the sleeve opening downward. The lid is secured to the furnace by two small screws. With the pyrex cap of the source end of the mass spectrometer tube envelope removed, the loaded furnace may be lowered into place on the "A" plate of the source plate assembly (Fig. 1), (Fig. 2,d). Two studs on the "A" plate (Fig. 2,s) determine the position of the furnace.

Figure 1 shows the furnace mounted in such a manner that emergent vapours pass directly into the ionizing chamber of the source. The nickel sleeve acts as the heating element of the furnace. Power is brought to the loaded sleeve through 0.040" copper leads a joining the upper terminals of the small press seels (Fig. 2,d) to a two wire press seel in the source end of the mass spectrometer tube envelope.

Power for the furnace is supplied by the output of a low voltage transformer (Hammond 1154), fed from a 25 cycle, 115 volt power line through two Variacs connected in series. The lower portion of the furnace projects through the two in order that there be no electrostatic disturbance of the ion accelerating potential or the ionizing electron beam by the A.C. supply of the furnace. One end

of the furnace heating element is connected electrically to the "A"

plate. The furnace, therefore, floats at the accelerating potential

level and as a result must be well insulated from ground. Variacs

being autotransformers do not provide this insulation whereas the low

voltage output, high voltage insulation transformer does. The series

Variacs permit course and fine adjustment of the furnace temperature.

Residual gases in the mass spectrometer tube do not in general interfere unless they give rise to ions in the mass range to be studied. However, if the pressure due to residual gases is too great, serious scattering of the ion beem and hence poor resolution will result. Following an analysis the furnace box is thoroughly cleaned. Also the nickel sleeve and plugs are discarded and a new assembly employed for each consecutive semple. These precautions eliminate the possibility of contamination by previous samples. The mass spectrameter tube envelope is wound with a heating element for "baking" purposes. The tube may thus be kept at temperatures up to 400°C. for any desired "baking" period. There is a pyrex cap at the source end joined to the main envelope by a 50/50 ground glass joint using Apiezon black vacuum wax at the interface. A moistened towel keeps the temperature of the Apiezon wax below its melting point and so maintains a vacuum seal at the ground gless joint during "beking". If the pressure due to residuel gases in the tube is low and the mass range in question is free of residual ions. the "baking" process may be omitted. It is necessarily omitted when the temperature involved is sufficient to cause the vapourization of the sample. In this case, it is necessary to evacuate the tube without "baking" to a pressure whene scattering of the ion beam due to residual gases is negligible. Before each analysis the instrument is checked for residual ion currents due to tube contemination or residual gases.

Tons of different masses are brought to a focus on the collector by varying the current through the coils of the focussing electromagnet. The ratio of the potential between "A" and "J" to that between "A" and "C" is constant for all values of the accelerating potential "A" to "C" (Fig. 1). This arrangement reduces the analyzer mass discrimination to a minimum (46,47) for those cases where it is necessary to use different accelerating potentials in order to study the isotopes of a particular element in several mass range. e.g., U , UCl , UCl , UCl , UCl , and U

RESULTS

Uranium Tetrachloride.

A sample consisting of 15 milligrams of UClh was placed in the furnace and the mass spectrometer tube was thoroughly "baked". Steady ion currents of the order of 10-13 superes corresponding to U were obtained continuously over a period of six hours. Poor resolution persisted for all settings of accelerating and focussing variables. This was attributed to the fact that considerable scattering was taking place. This scattering was probably due to the degassing of the UUlh. Good resolution was obtained with a similar sample which had been dessicated before being placed in the furnace. A value of 138 ± 3% for the ratio U238/U235 was calculated from U fon current measurements made on this sample. The results obtained with small samples (1 mg.) were unsatisfectory because of the difficulty in handling UClk which is hygroscopic. However, UCli and other hygroscopic materials can be used if kept at all times in a dessicated atmosphere. It has been suggested that these hygroscopic compounds be prepared in the furnace after the system has been dried and degassed.

Uranium Tetrafluoride.

With milligrem semples of UF_h no ion currents corresponding to U⁺, UF⁺, UF₂⁺, UF₃⁺, or UF_h⁺ were detected until the furnace attained relatively high temperatures. At these temperatures there were detected UF₂⁺, UF₃⁺ and UF_h⁺ ion currents which increased in magnitude as the furnace temperature was raised but disappeared completely before becoming large enough to permit accurate measurements being made. After several such samples had been tested it became obvious that the accelerating potential was being shorted out. Either excessive heat from the furnace

or sample condensation caused the pyrex spacers of the source plate assembly to become conducting. This placed a high resistance short circuit from "A" to "C" (Fig. 1) thereby changing the accelerating potential value and causing the disappearance of the ion currents.

Cuprous Chloride.

Copper isotope abundance measurements were made on two samples of CuCl from the same source (Merck Reagent). Steady and well-resolved Cu⁺ion currents of 10⁻¹² - 10⁻¹³ ampere magnitude were recorded graphically with a Leeds and Northrup Speedomax recorder. From this data Cu⁶³/Cu⁶⁵ isotope abundance ratios were measured. Table 4 gives the results of these measurements:

Table 4
Copper Isotope Abundances

	Sample	2	Ion Studied	Cu ⁶³ /Cu ⁶⁵ Ratio	Precision
Merck	Resgent	CuCl	Cu+	2.293	±0.002
**	**	69	**	2.294	±0.001

Average 2.294 ± 0.002

Each abundance ratio represents the average value calculated from eight pairs of Cu⁶³ and Cu⁶⁵ ion current peaks as recorded by the Leeds and Northrup Speedomax. (Table 5) shows the copper isotope abundance ratios as determined by other investigators.

Table 5

Copper Isotope Abundance Ratios

*******	Investigat	or	Cu63/Cu65 Ratio
	Inghrem	(48,49)	2.235 ± 0.010
	Dempster	(50)	2.229 ± 0.033
	Cameron and White	(1)	2.220 ± 0.020
	Eweld	(51)	2.330 ± 0.030
	Duckworth and Hogg	(52)	2.277 ± 0.017
	This work		2.294 ± 0.002

Average 2.264

DISCUSSION

Other experimentors have reported similar difficulties in connection with small samples of hygroscopic substances such as UClh.

To obtain 10-13 ampere ion currents from UFL a temperature above that at which the furnace can operate satisfactorily is necessary. Others have reported similar difficulties concerning the operation of ion sources at high temperatures (1)...(16). In each case the maximum temperature is different depending on the nature of the source. Samples, such as CuCl, which are not hygroscopic and have appreciable vapour pressures below 1000°C are easily handled and investigated mass spectrometrically. Although the precision of the copper abundance measurements is better than 10.1 percent the absolute accuracy is probably no better than ±1.0 percent.

The furnace used is capable of producing ion currents of sufficient magnitude for the mass spectrometric analyses of any sample which melts, decomposes or sublimes, provided the sample has a vapour pressure of 10⁻³ mm. in the liquid or solid state at a temperature in the range 50° - 950°C. If arrangements are made to load and mount the furnace in a dessicated atmosphere, hygroscopic samples may also be studied.

TABLE (1)

Sex	ple	Ion Studied	Vepour Pressure	at which pressure de (in C°	vepour termined	Melting Point (in C°)		g Point
AgC1	(1)	Ag+	3.7	882		455 ^x		1550×
Ba	(2)	Be ⁺	10-3	701.1		850		1140
Ве	(3)	Be ⁺	7.6 x 10-4.5	1077	(53)	1350		1500
Ca	(4)	Ca ⁺	10-3	529		810		1170
Ср	(5)	CP ⁺	*			1950		2900
ca	(6)	ca	10-3	219.1		312		767
CaI ⁵	(7)	ca ,car ,car2				388		713
CaC12	(1)	Cd	3.0	618		568		960
Co	(5)	Co ⁺	10-3	1254		1480		3000
CoCl	(8)	Co ,CoCl				subl.		1049
CrCl ₃	(1)	Cr+					subl.	1300
Cu	(3)	Cu ⁺	10-3	1320		1083		2300
Cu ₂ Cl ₂	(1)	Cu ⁺ ,CuCl ⁺	1.0	500	(40)	422		1366
Pe	(9,11)	Pe ⁺	1.0	1884		1535		3000
FeC12	(1)	Fe ⁺				670		subl.
Ge	(5)					1900		

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			remperation at which	Temperature which vepour		
	Ion Studied	Vepour Pressure (in mm)	pressure d	determined Co)	Melting Point (in Co)	Boiling Point (in Co)
3	To the	7.7 × 10-4	815	(42)	150	1450
3	In				subl. 586	volet. 600
(5)					2350	884 人
(9)	M	10-3	162.3		62.3	760
3	Lit	5 x 10-2	930	(34)	186	
(3)	1114					
(3)	* 84 ± 84	10-3	216		651	0011
(5)	Mr, Mr, Mr	10-3	198		1260	1900
(00)	Mo ⁺	10-3	2293		2620	3700
(21)	Mo				d. 150	
(2)	No.	10-3	238		97.5	880
(33)	+ 388	10-3	1250		1773.5	4300
(3)	M1+				en i.	973
(2)	Pb, Pbc1	1.7 × 10-3	3		20	056
(21,41)	Pb, PbI, PbI2	10-2	300	((43)	100	356
(2)					1553	5200

Sample	9	Ion Studied	Vapour Pressure (in ma)	remperature et which vepour pressure determined (in Co)	vapour termined	Melting Point (in C ^O)	Boiling Point (in Co)
4	(5)		10-3	2080		1455	2900
2	(9)		0.75	306	(44)	38.5	700
Repor	3	Re+				c.e. 220	subl. 450
a	(5)					1985	> 2500
8	3	+ 0S	1.0	818		630	1380
Sucle	(5)					945	623
b	(2,5)	+200	10-3	713.4		800	1150
HF3	(1)	*133+				d. 400	
TI	(2)	11	10-3	112.7		302	1457
der.	(97)						volat.
מסול	(97)					subl.	618
N(00)6	(35)	N.				4. 100	
Zn Zn	(9)		10-3	296.3		4.9.4	106
ZnI2	(7)					944	459

Mall melting and boiling points and all vepour pressures with their temperatures, unless otherwise indicated, are taken from: Handbook of Chemistry and Physics, Chemical Rubber Pub. Co., 31st Ed., 1947.

TABLE (2)

Sample		Ion Studied	Temp.	Filement	Menner in Which Thermionic Source Prepared
A1203	(17)	A1	1500	tungaten helix	coated with sample- weter binder
BaO	(18)	Be+		tungeten	costed with sample
(Be0)(Al ₂ 0 ₃)(8102)(17,23)	Be [†]		tungsten heliz	coated with sample- water binder
CaO	(30)	Ca ⁺		pletinum	costed with sample
(CeO)(Al2O3)(8	8102)(17,19)	Ca ⁺		tungsten helix	coated with sample- water binder
Ce ₂ 0 ₃	(21)	CeO	1000	tungsten	coeted with cerium in nitric acid solution converted to CeC2 by application of heat prior to emission.
Ce ₂ O ₃	(17)	CeO		tungsten helix	costed with sample- water binder
Cr	(9)	Cr+	1200	tentelum	furnace containing small amount of Cr metal.
Fe	(55)	Fe [†]		platinum	wire electropisted with sample
Ge ₂ 0 ₃	(53)	Ga	1800	platinized tungeten	costed with sample
*	(17)	Ga ⁺	1800	tungsten helk	coated with sample- water binder
In203	(17,18)	In	900	tungsten	coated with sample
**	(23)	In		platinum foil	
K	(24,28)	K+		tungsten	nitrates of K and Fe fused, ignited and re- duced in H2 then pounded in grooves of a MgO tube surrounded by a helix.
(K20)(Al203)(E	3102) (56)	K+		pletinum	coated with sample
La ₂ 0 ₃	(51)	LaO	1600	tungsten	costed with sample in nitric scid solution.

TABLE (2), cont'd.

Semple		Ion Studied	Temp	Filsment	Menner in Which Thermicalc Source Prepared
Li	(27)	II,	760	platinum disc	impregnated with sample
(1120)(A1203)(S102)(19,26)	L1 ⁺		platinum strip	peinted with sample- water binder
	(1 7)	M ⁺	-tu	tungsten helix	costed with sample- water binder
(MgO)(Al203)(8102)	(19)	Mg ⁺		platinum strip	painted with sample- water binder
	(17)	Mg ⁺		tungsten helix	costed with sample- water binder
MnO	(17)	Mn ⁺		tungeten halix	coated with sample- water binder
Na ₄ P ₂ O ₄	(50)	Na ⁺		pletinum	ccated with sample
Rb	(27)	m'	600	platinum disc	impregnated with sample
(Rb20)(Al203)(S102)	(26)	Rb+			
SrO	(18)	Sar+		tungsten	costed with sample
(Sro)(Al ₂ 0 ₃)(S10 ₂)(1	7,23)	8r ⁺		tungsten	costed with sample- water binder
T1203	(17)	T1 ⁺		tungeten	coated with sample- water binder
v ₂ o ₃	(17)	v+		tungeten	coated with sample- water binder
Y203	(17)	¥+		tungsten helix	coated with sample- water binder.

TABLE (3)

Samples Studied with Mass Spectrograph using Spark Source

F2.61	<u>sent</u>	Nature of Spark Source Employed
Al	(29)	Inductively coupled H.F. oscillating spark between a
Al	(30)	Aluminum cathode in meon discharge tube.
Au	(29) (34)	Inductively coupled H.F. oscillating spark between gold electrodes - i.e. "Dempster Spark Source".
Ве	(59)	Dempater Spark Source - Be electrodes.
Ca	(30) (31)	Cd cethode in meon discharge tube. Cd in well in cethode of discharge tube.
Ce	(32)	Dempster Spark Source - Nickel tubes with oxide of cerium and reducing agent as electrode.
Cu	(29)	Dempater Spark Source - Copper electrodes.
Dy	(32)	Dempster Spark Source - Nickel tubes with oxide and reducing agent as electrodes.
Er	(32)	Dempater Spark Source "
Gd	(32)	Dempster Spark Source "
Hf	(33)	Dempster Spark Source - Nickel tubes of the metal and its oxide as electrodes.
Li	(29)	Dempater Spark Source - Li electrodes.
Lu	(33)	Dempster Spark Source - Oxide plus tentalum in mickel tubes as electrodes.
Na	(32)	Dempeter Spark Source - Nd electrodes.
N1	(29,35)	" - N1 electrodes.
Pd	(34)	" - Pd electrodes.
Pt	(29)	" - Pt electrodes.
Sa	(35)	" - Oxide end reducing agent in nickel tubes as electrodes.
Se		Se in well of cathode in discharge tube.
Sn	(29)	Dempster Spark Source - Sn electrodes.
Ta	(33)	" - Te electrodes.
Te	(36)	Te in well of cathode in meon discharge tube.

Teble (3), cont'd.

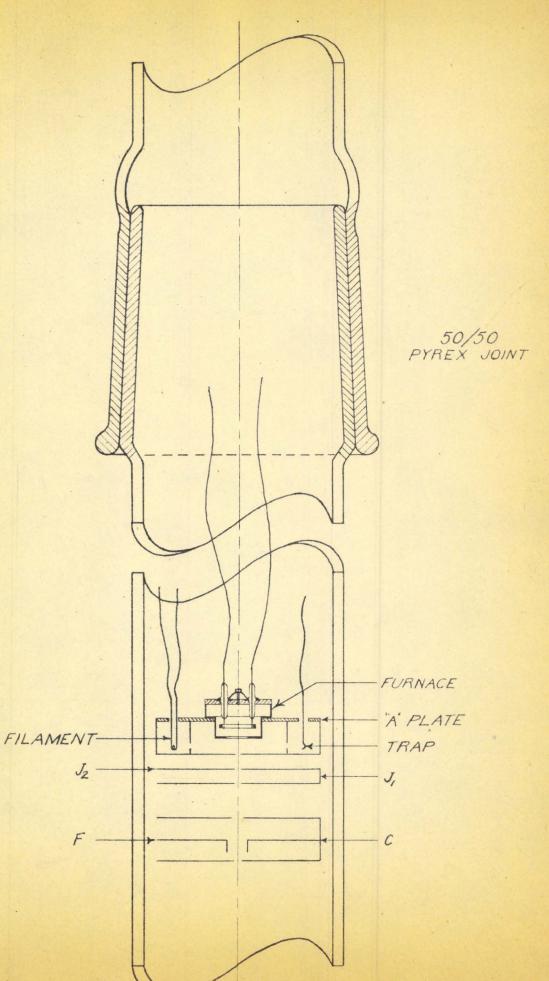
Eleme	nt	Neture of Spark Source Employed.
Th	(37)	Dempsters Spark Source - Sn and Th electrodes.
U	(37)	" - Au and U electrodes.
W	(29)	" - W electrodes.
Y	(33)	- Mixture of Yttrium oxide and lanthamum metal as electrodes.
Ap	(32)	Dempster Spark Source - Oxide plus reducing agent in nickel tubes as electrodes.
Zn	(30)	Zn cethode in meon discharge tube.

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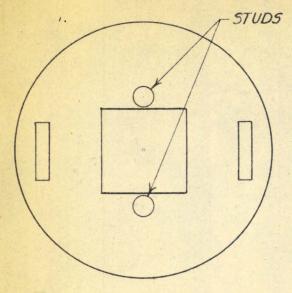
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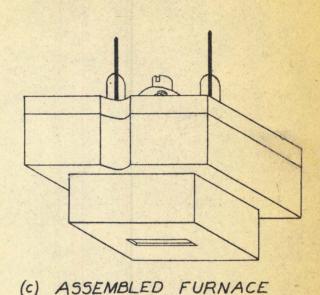
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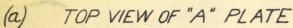
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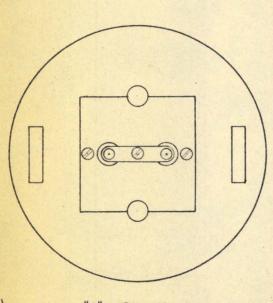


FIC 1









SPRING CLAMP

SAMPLE

O.040" NICKEL
SLEEVE & PLUGS

(b) "A" PLATE WITH FURNACE MOUNTED

(d) INTERNAL VIEW OF FURNACE