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CONCLUSIONS <p>Covers the application of the General Electric Ion Resonance Mass Spectrometer to the problems of Power Tube Development.</p>		

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APPLICATIONS OF THE MASS SPECTROMETER TO TUBE DEVELOPMENT

BY

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INTRODUCTION

The problem of gases in power tubes is one of the most critical problems in the industry today. Many of the difficulties encountered in producing long-life tubes are caused by prolonged gas evolution from tube parts throughout life. The future points to a demand for smaller tubes operating at temperatures as high as 400 to 800°C and perhaps under dense nuclear radiation. This being the case, the gas transparencies of all materials must be considered and indeed may be the cause of rejection of a given material for such high-temperature tube use even though its electrical and mechanical properties are excellent.

In addition to the above needs there exists a tremendous requirement for a more basic insight into the gaseous decomposition products of many reactions which take place in normal tube processing. A knowledge of the composition of the gases evolved during bakeout and exhaust is necessary to supplement pressure measurements in order that time and temperature schedules can be set to remove unwanted gases. Realizing these urgent needs, a program was set up in the General Electric Power Tube Department to improve the reliability, uniformity, performance, and life of power tubes by investigating the gases evolved during many different phases of tube manufacture. The mass spectrometer was chosen for use in this program because it offered an excellent method of carrying out the above analyses. In general, the gas pressures encountered in tube work are below one millimeter and the quantities of gas are small. This is ideal for the mass spectrometer which is capable of monitoring small samples of gases at very low pressures. For our purposes a compact, relatively portable instrument was desirable so the General Electric Ion Resonance Mass Spectrometer was chosen. This is a limited-range instrument capable of focusing, with unit resolution, ions from mass two through 70 and, with somewhat less resolution, ions up to mass 120. The instrument has proved very satisfactory for our purposes since 90% of the analyses utilized only the range up to mass 50.

ANALYTICAL SETUP

A sampling system was developed which is especially suited to the types of analyses we make. See Figure 1. It consists of two sampling systems, each directly linked to the mass spectrometer or to each other by a three-way hollow plug stop-cock. One system is of conventional batch-type design and accommodates samples at pressures up to atmospheric by providing successive reductions in pressure through the expansion of small volumes into larger ones. The normal pressure ahead of the molecular leak into the mass spectrometer is kept below 50 microns. The second system allows continuous sampling directly into the mass spectrometer during vacuum degassing or tube exhaust. These two sample systems utilize two independent pumping systems in addition to the primary mass spectrometer vacuum system. Figure 2 shows the layout of the systems.

When a batch sample is being analyzed the continuous system can be isolated from the mass spectrometer while it is being used to evacuate a sample prior to another analysis. Either system can be connected to augment the pumps in the other system. If the pressure in the continuous system rises above limits for the mass spectrometer the gas is expanded into the three-liter expansion volume of the batch system and the analysis is then made from this reservoir. Although the stop-cocks definitely limit the ultimate pressure in the system, they add greatly to its versatility. The system is normally operated untrapped and pressures of 1×10^{-5} mm Hg are readily attained. Heating tape is used to warm the glass to 200°C and the stop-cocks to about 80-90°C since Apiezon T stop-cock grease is used. This gives good outgassing and prevents adsorption from the sample onto the walls of the system.

SAMPLING SCHEMES AND DEVICES

Various schemes have been developed to accommodate the various sampling requirements. Many of these are based on those developed by Dr. F. J. Norton of the General Electric Research Laboratory during his years of work in this field. Some of the exhaust stations in our exhaust section have been adapted so that the mass spectrometer can be used to analyze gases being evolved during tube exhaust. The mass spectrometer and its associated equipment have been designed for portability. The equipment is easily rolled on dollies and quick disconnects and flexible lines are provided for the water supply. A twelve inch long, two inch diameter stainless-steel bellows allows quick connection to the

vacuum lines of the system. The large exhaust sets and high power supplies required to operate power tubes on exhaust demanded that the mass spectrometer be moved to the exhaust station for analysis. Whenever possible, however, samples are taken in sealed bottles and brought to the spectrometer laboratory for analysis. For non-critical analyses which can be quickly run on the mass spectrometer 250 ml bulbs with stop-cocks are used. See Figure 3A. Two-liter glass bottles, which can be sealed off and broken under vacuum by means of a break-off seal and metal plunger, are used for low pressure samples. See Figure 3B. One-liter micron of gas provides sufficient quantity for a good analysis, hence sample pressures in the order of one-half micron can be handled in this volume.

As mentioned, one of the main areas of interest is the determination of the gaseous products evolved from materials under vacuum at elevated temperatures. For this work a quantity of the material is heated in a quartz tube by means of an electric oven under vacuum. The quartz tube is outgassed at temperatures approximately 100°C higher than the sample is to be heated prior to magnetically moving it into the hot zone. Non-magnetic samples are moved by means of glass encapsulated ferrico slugs in the vacuum system controlled by external magnets. The slugs are removed from the hot zone prior to the start of the analysis to eliminate any contribution they may have to the analysis. The pyrex tubing up to the spectrometer tube is heated during analysis. Normally the pumps are shut off from the system while the temperature of the sample is raised in 100°C increments. The quantity of gas evolved during each 100°C step is determined by measuring the total pressure in the known system volume. At the end of each step the sample is opened to the mass spectrometer and analyzed if the pressure is low enough. Otherwise, it is expanded into the three-liter batch volume and analyzed from there. In this case, the continuous sampling system is pumped out and the next temperature increment is started while the previous analysis is being made. Much the same scheme is used for analyzing the gases evolved from the exhaust of small tubes and from filament operation.

Of primary interest is the determination of gases in tubes which have been operated and which have given erratic performance or found to be gassy. The determination of the gases present often leads directly to, or at least gives a clue to, the gas source. Some devices for opening completed tubes under vacuum are shown in Figure 3. For small ceramic or glass tubes the stainless-steel tube, shown in Figure 3C is used. The sample is inserted in the open end of the metal tube which is then welded shut. The enclosure is then evacuated and removed from the system under vacuum by closing the vacuum stop-cock.

The thin-walled, stainless steel tube is then squeezed in a vise until the sample tube therein is fractured. Care must be exercised to provide sufficient metal length so that the glass-to-metal seal is not cracked during this operation. The assembly is then reattached to the mass spectrometer vacuum system and the gas sample is analyzed.

For larger tubes the devices shown in Figure 3D and 3E are used. Both employ a metal plunger which can be raised magnetically and dropped so as to fracture some relatively vulnerable area of the completed tube. The enclosures are sealed to the tube with hard-vacuum wax and evacuated as before. In the case of the glass enclosure, Figure 3D, which is used when planar surfaces are to be broken, the system is evacuated and the tube is fractured while attached directly to the system. A 1/8-inch thick ceramic is easily broken by a 300-gram plunger with a case-hardened point dropped through a distance of about two feet. The metal enclosure, Figure 3E, is employed when curved-glass seals or ceramic are to be broken. In this case the impact of the plunger and subsequent seal fracture has been found to break the glass enclosure. The assembly is attached and evacuated as described and then sealed off and removed under vacuum. The tube and metal assembly are then rotated to allow the plunger to slide down to the glass end of the enclosure. The plunger is held there by a magnet while the arm is raised to the vertical position and then the plunger is dropped to fracture the seal.

On large, extremely rugged tubes the metal tubulation oftentimes offers the most vulnerable spot for opening. These tubulations are usually copper or nickel which have been pinched off to a razor sharp edge by cold welding. To open these tubes another device (not shown) is used to enclose the tubulation and, after evacuation, a sharp edge is forced through the tubulation by means of a bellows arrangement.

AREAS OF INVESTIGATION AND RESULTS

Many investigations have been carried out on gas samples from large mercury arc rectifiers. See Figure 4. Little is known about the clean-up of gases in the arc discharges. To date a great deal of care has gone into the degassing of these devices during exhaust. However, it is now believed that even a well gassed, reasonably leak-tight, pumpless rectifier owes its long life to the tremendous ability of the arc discharge to clean up gases during operation. Mass spectrometer analysis has revealed many interesting facts about the nature of the clean-up and the gases found in these tubes. Some analyses have revealed that the gas in the tube at initial test is primarily water vapor. Others have indicated the presence of an abundance of hydrogen. Both

of these results pointed to the need for improved bakeout.

It is known, and mass spectrometer tests by Dr. Norton have clearly shown, that hydrogen ions produced by corrosion of mild steel easily penetrate the steel and result in hydrogen pressure buildup inside a tube. This was a problem in rectifiers using mild steel inner and outer tanks between which cooling water was circulated until it was found that a solution of 0.1% of sodium chromate in the water prevented corrosion. Recently a pumpless rectifier with a mild steel inner tank was returned from the field because it displayed high arc drop under load in parallel with other rectifiers. A sample taken from this tube revealed that 55% of the gas was hydrogen and 45% water vapor. It was suspected that corrosion had caused hydrogen ion penetration which produced the hydrogen in the tube. Figure 4A clearly shows the correctness of this conclusion.

The hydrogen ion penetration problem has been solved in pumpless rectifiers by using stainless steel inner tanks which resist corrosion. However, even with stainless steel, large quantities of gas must be removed during initial processing to insure reliable long-life tubes. The mass spectrometer is proving a very valuable tool for increasing our understanding of the mechanisms involved and guiding the future investigational work.

A great deal has been learned about the ability of the arc discharge to clean up air as well as other gases. A tube which has developed a small air leak during operation will differentially clean-up the components of air. Typical analysis of some rectifiers which have been operated with an air leak are shown in Figure 5. The device displays a tremendous ability to clean up oxygen and a lesser ability to clean up nitrogen resulting in a high concentration of argon which makes up only about one percent of normal air. Argon is peculiar in that it displays a low dc arc drop on the test normally used to check the vacuum in a tube giving a false impression of good vacuum. Nevertheless, a few percent concentration of this gas in a tank will cause serious arc backs. By means of the mass spectrometric analysis the tolerable argon limits have been established. By knowing the gas pressure in the tank and analyzing the percentage of argon it can be determined whether the leak occurred over a long period of time or not. It has been found that a tank which has developed a leak on standby, after operation, also displays similar differential gas clean-up provided a very limited quantity of air has leaked in. This clean-up is thought to be the result of adsorption by the clean graphite and also by the clean steel walls which have been wet with mercury from the arc discharge. Work is continuing in this area

with the aim of continuing to increase reliability and rectifier tube life through a better understanding of the gas evolution and clean-up phenomena taking place therein.

Another investigation was carried out on a small metal-ceramic high-frequency triode tube. See Figure 6. Cathode emission was not up to expectations and poisoning was apparent after a few hours of life. Erratic grid control characteristics were also experienced. This tube was easily exhausted on the mass spectrometer's continuous sampling system and an effort was made to duplicate the production exhaust schedules while analyzing the gases evolved. The gases evolved during bakeout were investigated as well as those evolved during getter degassing, cathode sintering and getter flashing. Single peak monitoring is easily accomplished on the General Electric Ion Resonance Mass Spectrometer and the evolution of various gases has been followed continuously throughout bakeout by this means. At constant pumping speed and linear oven temperature rise the variation in the peak height of the gas is a function of the amount of the gas being evolved. Water vapor is an illustrative example. Figure 6A shows a graph of the water vapor peak as a function of oven temperature. The increase at 60-70°C is a result of loosely held surface adsorbed water. A rise in the 200°C range seems to be characteristic for all ceramic-metal tubes and is due to water which is more tightly bound, perhaps chemisorbed, being released. The increase at 400°C and above has also been found when degassing glass and it is concluded by some to be caused by actual chemical decomposition.¹ Some other extremely interesting results were obtained, the most significant being a predominance of carbon monoxide during cathode breakdown and an evolution of gas from the getter flash. This tube has a conventional oxide cathode formed from the decomposition of co-precipitated triple carbonates during exhaust. The main product from the carbonate decomposition should be carbon dioxide rather than carbon monoxide. Results taken on this tube showed that the main product of decomposition of the carbonates was carbon monoxide which was three to four times more abundant than carbon dioxide. It was known that the exhaust on the mass spectrometer was more complete than on the production exhaust system and, therefore, it was logical to assume that carbon monoxide could be evolved in finished factory tubes. This strong reducing agent, if present, would reduce the barium oxide present in the cathode and cause excessive

¹ S. Dushman, Scientific Foundations of Vacuum Technique, J. Wiley, 1949

barium evaporation to the grid. Indeed, tubes opened after a few hours life showed grids contaminated with barium. Hydrogen was evolved to some degree at the time of breakdown and it has been reported that its presence does cause the carbonate to decompose yielding predominately carbon monoxide; however, it was felt that this did not explain fully its over abundance. Therefore, a program was carried out which systematically eliminated possible sources of carbon monoxide. A tube without cathode coating was analyzed and the large quantity of carbon monoxide again was shown. The next tube analyzed contained no cathode structure whatsoever and again the same results were experienced. Another effect presented itself, however, and that was the evolution of hydrogen at temperatures above which the carbon monoxide was removed. This effect is referred to later. It had been noted that the evolution of carbon monoxide followed very closely the application of heater power. This eliminated the possibility of other components being heated by radiation and evolving gas and linked the gas directly to the heater. The heaters used in this tube are 3.8 mil tungsten coated with alumina, and then hydrogen fired at 1200°C to set the coating and burn off the binder. Subsequent analysis of the gases evolved from groups of heaters mounted in a separate bulb revealed that large quantities of carbon monoxide were released at the same power at which cathode breakdown occurred in the completed tube. Large quantities of hydrogen were also evolved as a result of the hydrogen firing. Hydrocarbons also released indicated that carbon-hydrogen reactions were taking place. A comparison of the gas evolved from two different lots of these heaters is shown in Figure 7. Subsequent testing showed that the heaters had to be heated to 1200°C in vacuum to remove all the gas. No significant quantities of gas were released above this temperature.

Great care must be exercised in degassing of getters because oftentimes the getter is flashed after the tube is sealed off. It has been shown by Dr. P. D. Zeman of the General Electric Research Laboratory that some getters not only give off gases when flashed but also that they evolve some gases which they themselves are incapable of gettering. With these facts in mind the normal getter degassing and flashing schedule was duplicated on the mass spectrometer. Hydrogen and carbon monoxide were the predominant gases evolved at the degassing step and hydrogen was released when the getter was flashed. In order to completely degas getters in general it has been found that they must be heated to just below the flashing temperature so that a small amount of material is actually evaporated.

Many samples of tube parts and sub-assemblies have been vacuum degassed and the products evolved analyzed. It is a customary practice in tube manufacture to hydrogen fire parts prior to assembling them in tubes. This procedure accomplishes a cleaning of the surface by reducing oxides and generally diffuses hydrogen throughout the material depending on the part thickness and the firing time and temperature. Parts so processed release large quantities of hydrogen when they are vacuum degassed. Other gases are also evolved, notably carbon dioxide carbon monoxide and water vapor. Figure 8 shows typical analysis. Investigation of a grid support cup which had been hydrogen fired at 1000°C for five minutes gave an analysis as shown in Figure 9. The low temperature results show clearly that this is a plated part and the plating solution is trapped during the plating process and is not completely driven off during the following hydrogen firing process. Gases were found to evolve from these parts at temperatures above those attained during tube exhaust. As previously mentioned, the presence of hydrogen was noted in a tube containing no cathode structure when the heater temperature was raised above that required to remove carbon monoxide. The quantity seemed too large to be entirely associated with the heater, and when grid structures outgassed under vacuum revealed little, a look was taken at the anode, a fairly large mild steel structure. A tube was exhausted and operated so as to bomb the anode excessively thereby raising the anode temperature. The composition of gas evolved as a function of anode temperature is given in Figure 10. The presence of hydrogen indicated that in the cathode-less tube the anode was being heated above normal and releasing hydrogen. Other testing has also shown that hydrogen is loaded into tube parts by hydrogen firing and during tube bakeout done in a hydrogen-nitrogen (forming gas) atmosphere. Unless extreme care is taken to heat those parts under vacuum at temperatures above that experienced in tube operation this hydrogen will be evolved during tube life causing series gas effects.

Ceramics play an important role in manufacture of power tubes as insulators, supports, and envelope materials. Since they have excellent electrical characteristics at high frequencies, good mechanical strength at elevated temperatures, and can be made vacuum tight they have replaced glass in many tube applications. Therefore, the gases evolved from these materials under vacuum is also under study. A typical analysis of the gases evolved from a commercially available ceramic is given in Figure 11.

In conclusion it may be said that the mass spectrometer has proved to be a very useful analytical tool in determining the gases evolved from the processing of tubes and tube materials. It is ideal for handling gases at the low pressures encountered in tube work and is easily adapted to many sampling procedures employing usual vacuum techniques. A real insight has been obtained into the composition of gases evolved during tube exhaust and indeed schedules and processing have been changed to accomplish much better degassing based on the results already obtained. "Bench Mark" spectrograms are now taken on tubes during periods of high yield. These are kept as references to pinpoint trouble areas if the yield drops at some future date. The future program calls for an expanded basic program to investigate the gas evolution of metals and ceramics as a function of the processing they receive. Close attention will be given to the breakdown of organic binders used in coatings, cathodes, cermets and ceramics. It is foreseen that the mass spectrometer will play as indispensable a role in future tube development as the mass spectrometer helium leak detector does today.

Only through such an extensive study of gases in materials can it be hoped to build power tubes capable of operating for long periods under the critical high temperature-high power demands of the future.

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October 11, 1956
Hotel Sheraton, Chicago, Illinois

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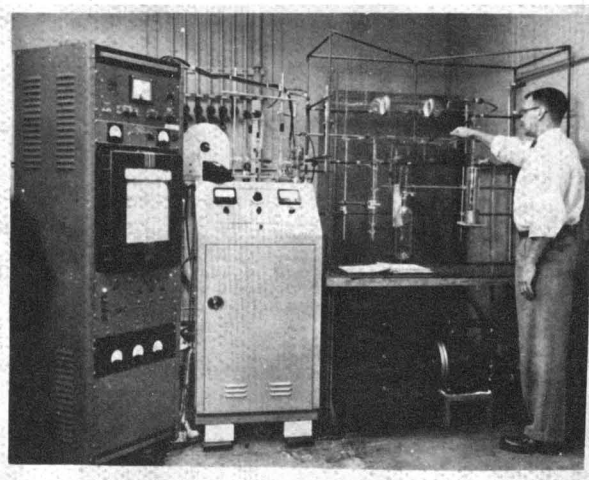


FIGURE 1

MASS SPECTROMETER AND SAMPLING SYSTEMS

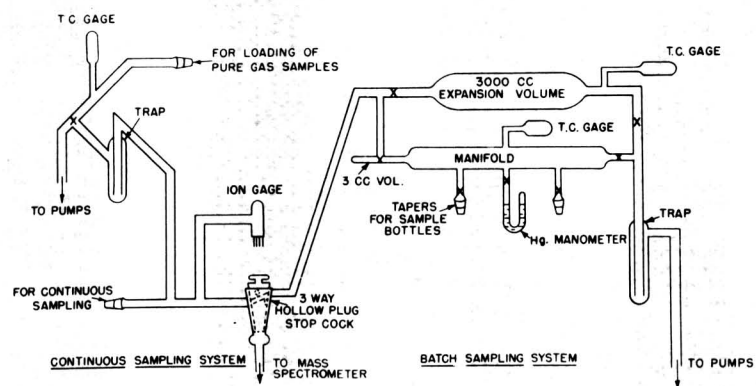


FIGURE 2
SYSTEMS LAYOUT

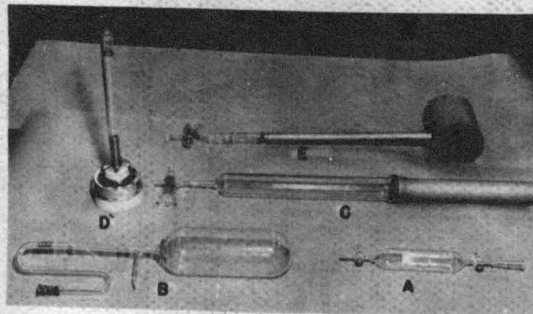


FIGURE 3

SAMPLING DEVICES

- A 250 ML SAMPLING BULB
- B 2L SAMPLING BOTTLE WITH BREAK SEAL
- C COLLAPSIBLE METAL TUBE CRUSHER
- D GLASS ENCLOSURE FOR OPENING TUBE UNDER VACUUM
- E METAL ENCLOSURE FOR OPENING TUBE UNDER VACUUM

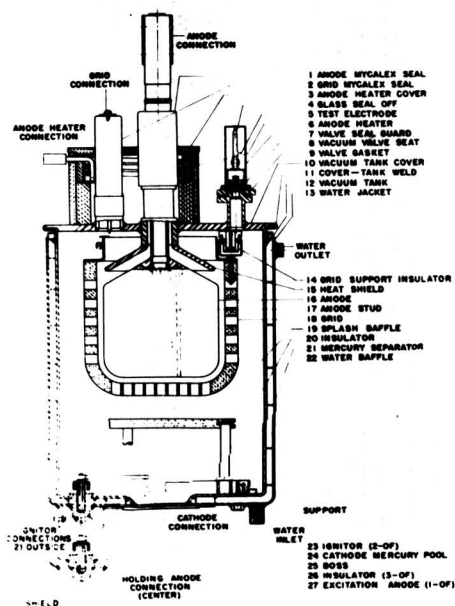


FIGURE 4

16" PUMPLESS IGNITRON RECTIFIER

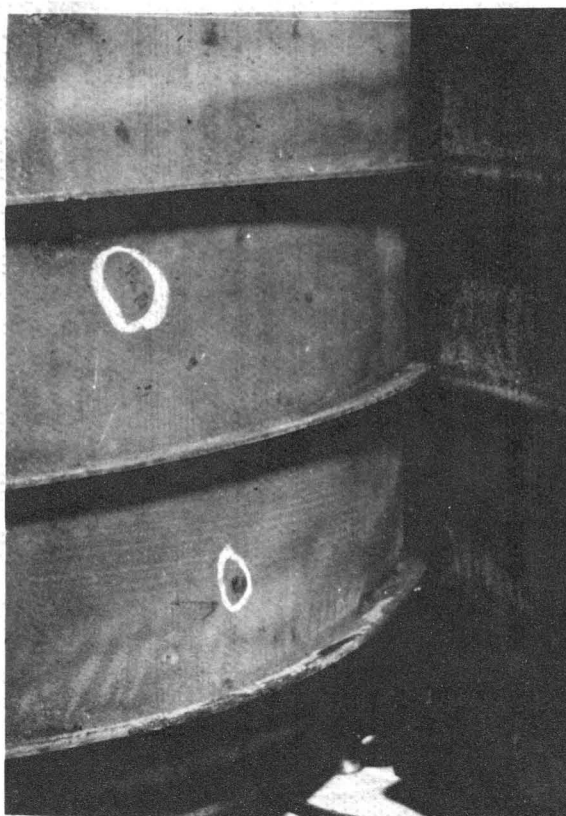


FIGURE 4A
CORRODED SURFACE ON TANK RECTIFIER

GAS COMPONENT	SAMPLE NO.		
	1	2	3
	MOL %	MOL %	MOL %
WATER VAPOR	-	2	TRACE
NITROGEN	94	88	95
OXYGEN	-	1	-
ARGON	6	8	5

FIGURE 5
TYPICAL ANALYSIS SHOWING DIFFERENTIAL
CLEAN-UP

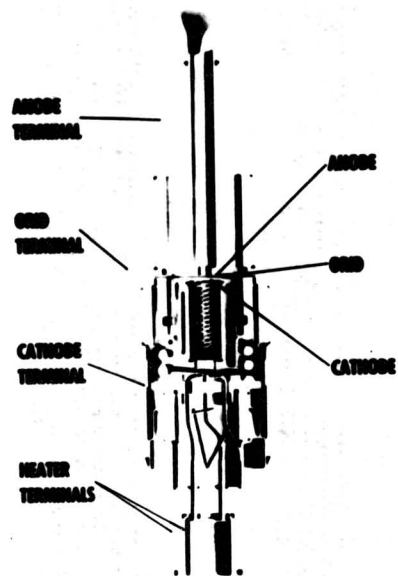


FIGURE 6
SMALL METAL-CERAMIC HIGH-FREQUENCY TRIODE TUBE

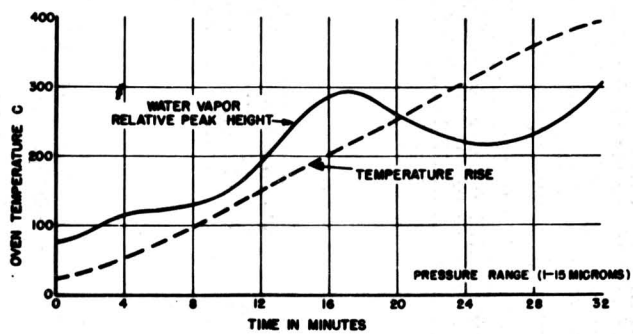


FIGURE 6A
WATER VAPOR EVOLUTION DURING BAKEOUT

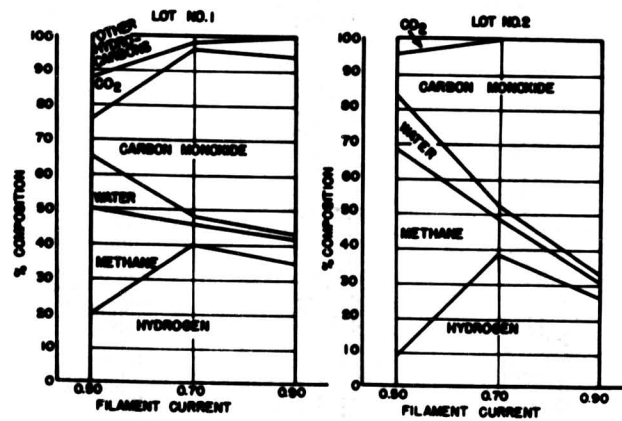


FIGURE 7
COMPOSITION OF GASES EVOLVED FROM ALUMINA COATED HEATERS

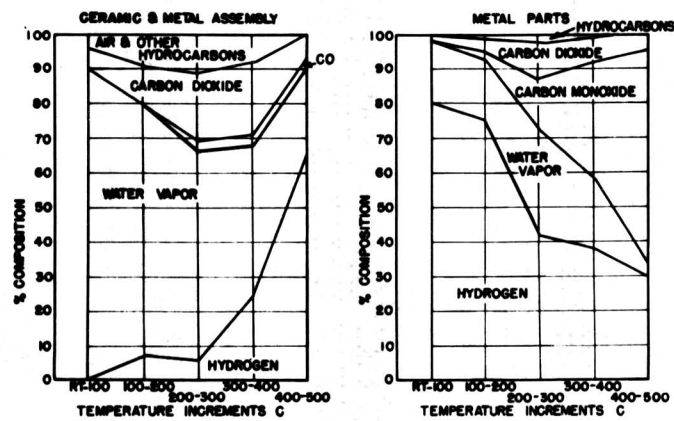


FIGURE 8
TYPICAL ANALYSIS SHOWING COMPOSITION OF GAS FROM TUBE PARTS

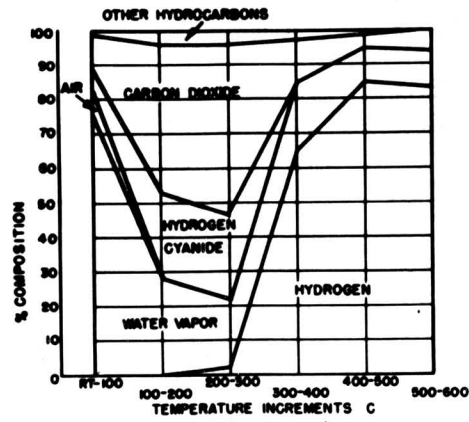


FIGURE 9
TYPICAL ANALYSIS SHOWING COMPOSITION OF GASES FROM SILVER PLATED PARTS

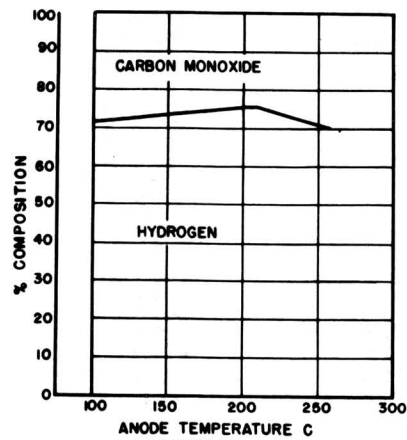


FIGURE 10
TYPICAL ANALYSIS OF GASES EVOLVED FROM ANODE UNDER BOMBARDMENT

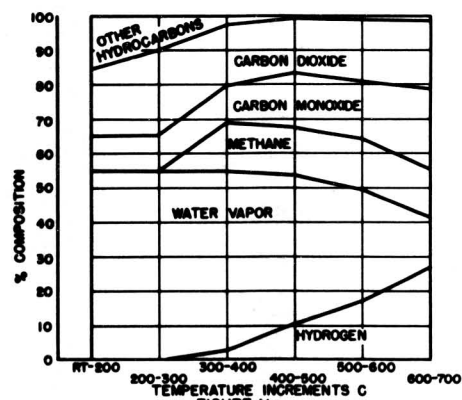
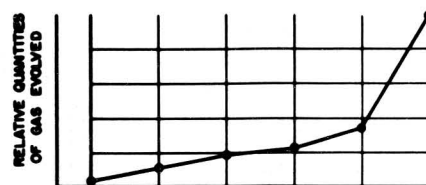


FIGURE 11
TYPICAL ANALYSIS OF GASES EVOLVED FROM A
COMMERCIALY AVAILABLE CERAMIC