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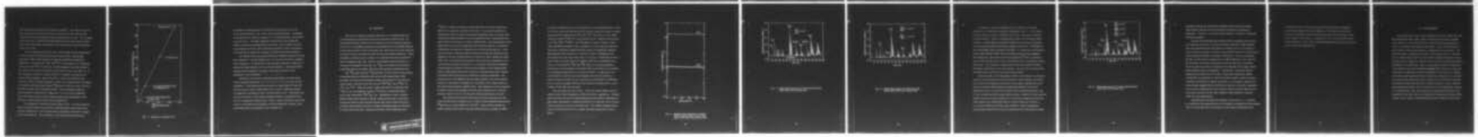

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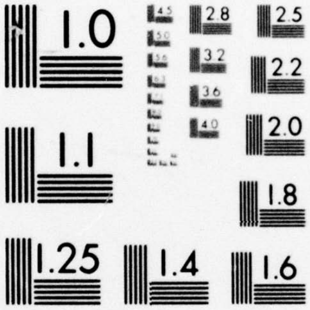
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REPORT SAMSO-TR-77-183

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# Ion Microprobe Analysis of Cathode Nickel Alloys

Prepared by F. M. WACHI, N. MARQUEZ,
and J. R. SHEPHERD

Materials Analysis Department
Materials Sciences Laboratory
The Ivan A. Getting Laboratories

October 1977

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This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

H. Wynne, Col., USAF
System Program Director, DSCS
Deputy for Space Communications Systems

FOR THE COMMANDER

Forrest S. McCartney
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An ion microprobe technique of analysis for manganese and other potentially detrimental impurities in machined cathode nickel alloy buttons is described. This nondestructive method does not jeopardize the subsequent performance characteristics of the nickel alloy pellet as a substrate for the barium-strontium oxide emitter material. This analytical technique is currently used as a standard quality assurance/quality control procedure in the fabrication of cathode assemblies of traveling-wave tubes for space applications.

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# PREFACE

The authors wish to thank J. H. Richardson and A. F. Young for designing the IMMA specimen fixture.

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# FIGURES

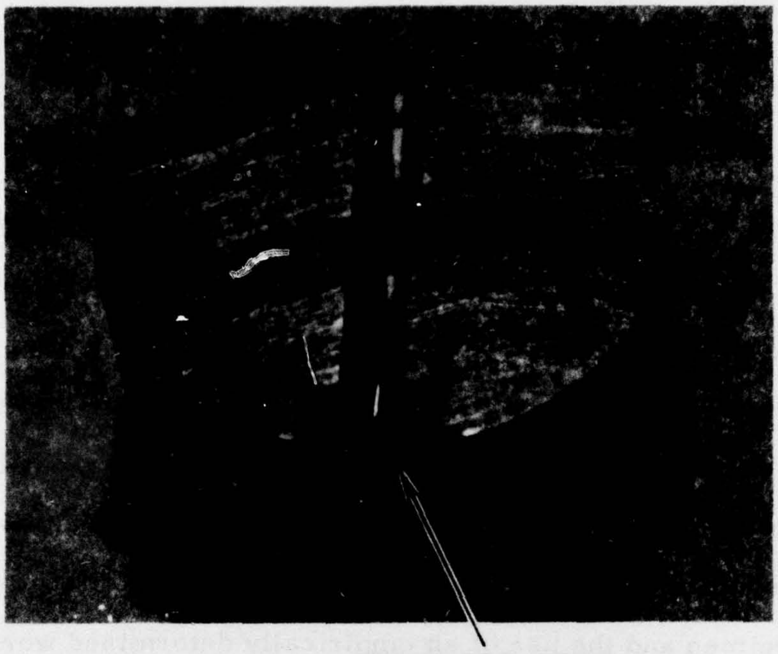
# I. INTRODUCTION

The need arose for a nondestructive method of analyzing the composition of cathode nickel alloys used in the fabrication of oxide cathode assemblies for traveling-wave tubes (TWTs) for space applications. The oxide cathode is the only active element in a TWT. Its activity, i.e., the level of electron emission and the length of time a given emission level can be maintained, determines the ultimate life of a TWT. Cathode activity is measured by the dip test technique [1]-[5]. It was recently discovered that the thermionic electron emission efficiency of oxide cathodes is seriously impaired by contamination of the high purity double-additive cathode nickel alloy by manganese. That is, the activity of the contaminated oxide cathodes is not only reduced markedly, but continually changes with time to render them inadequate for space TWT applications. The double-additive cathode nickel alloy, which contains controlled quantities of tungsten and zirconium, is the substrate for the barium-strontium oxide cathode emitter material. This paper describes an ion microprobe technique of analysis for manganese and other potentially detrimental impurities in cathode nickel alloys. This analytical method is used as a standard quality assurance/quality control procedure in the fabrication of cathode assemblies for space TWTs.

## II. ANALYTICAL METHOD

The ion microprobe mass analyzer (IMMA) used in the technique to be described is Applied Research Laboratories Model 101 000 [6]-[14]. The analytical method is based on the observation that the yield of sputtered ions from the sample is greatly affected by the surface chemistry of the sample, especially if it readily forms surface oxides. Hence, the technique involves the use of a reactive electronegative molecular ion, $^{18}O_2^+$, as the primary bombarding species to enhance and control the emission of sputtered ions from the specimen and the use of an empirically determined working curve to convert the sputtered ion intensities to a quantitative analysis for manganese.

Cathode material verification is conducted on machined cathode pellets before further processing steps in the manufacture of the oxide cathode assembly. The cathode buttons are cleaned with appropriate solvents upon receipt from the machine shop, dried, and mounted in a specially designed IMMA fixture fabricated from 270 nickel alloy (Fig. 1). The sample holder is constructed to provide an equipotential surface that will permit maximum collection efficiency of the secondary ions by the pickup electrode of the ion microprobe. Each fixture accommodates up to seven pellets (Fig. 2). Each cathode pellet is identified by the specimen holder number and its position relative to the spring clip. Electrical contact with the stacked cathode buttons is made with the stainless steel spring clip.



STAINLESS STEEL CLIP/
PELLET RETAINER

**Fig. 1. IMMA Specimen Holder**

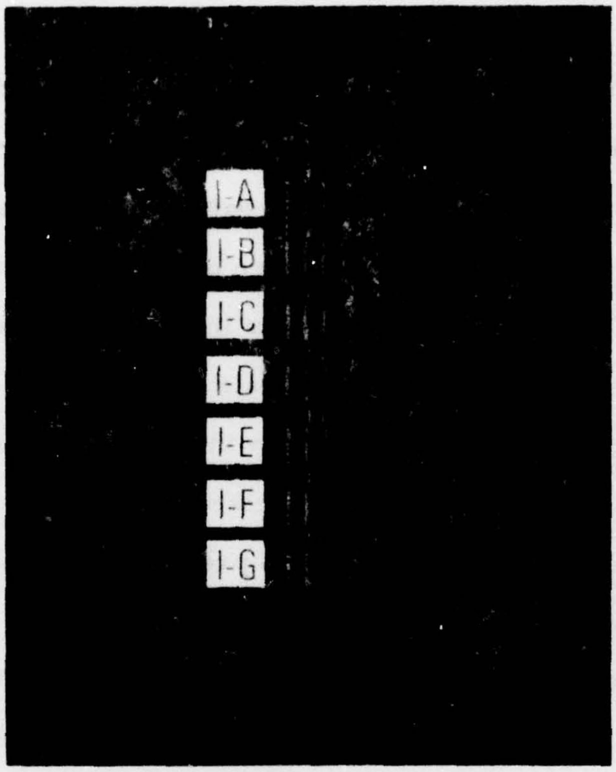


**Fig. 2. IMMA Specimen Holder with Seven Cathode Pellets**

After preliminary instrument adjustments, the $^{18}O_2^+$ ion beam is turned on only if the pressure of the specimen chamber is $\leq 8 \times 10^{-7}$ Pa, with the coldplate maintained at liquid nitrogen temperature. It is extremely important that the residual partial pressure of the ubiquitous $^{16}O_2$ gas be reduced to a very low level to minimize its interference with the manganese and zirconium analysis. During the analysis, the chamber pressure is held at $\sim 3 \times 10^{-5}$ Pa; leakage of $^{18}O_2$ gas from the anode aperture of the duoplasmatron ion source is responsible for the rise in pressure. The $^{18}O_2$ gas source pressure should be $> 8 \times 10^4$ Pa to prevent undesirable arcing problems in the ion gun.

Only a part of the outer cylindrical surface of the cathode pellet (Fig. 3) that does not form part of the curved surface of the Pierce electron gun is bombarded with energetic ions. An area 140 × 112 μm on the nickel alloy surface is bombarded with 20-keV $^{18}O_2^+$ ions at a beam current density of 0.13 mA/cm$^2$ for five minutes in the raster mode of operation. Subsequently, the scan dimensions are reduced so that the ion beam is rastered over an area 100 × 80 μm within the previously ion-etched region at a beam current density of 0.038 mA/cm$^2$. A mass spectrogram of the secondary positive ions emanating from this 100 × 80 μm area is then recorded over the mass range from 1 to 150 amu. Since residual surface contaminants from machine tools, residual hydrocarbon gases in the IMMA, and topographical effects could interfere with the manganese determination, a spot roughly the size of the ion beam diameter located within the previously rastered area (Fig. 4) is then examined by operating the IMMA in a point mode to ensure

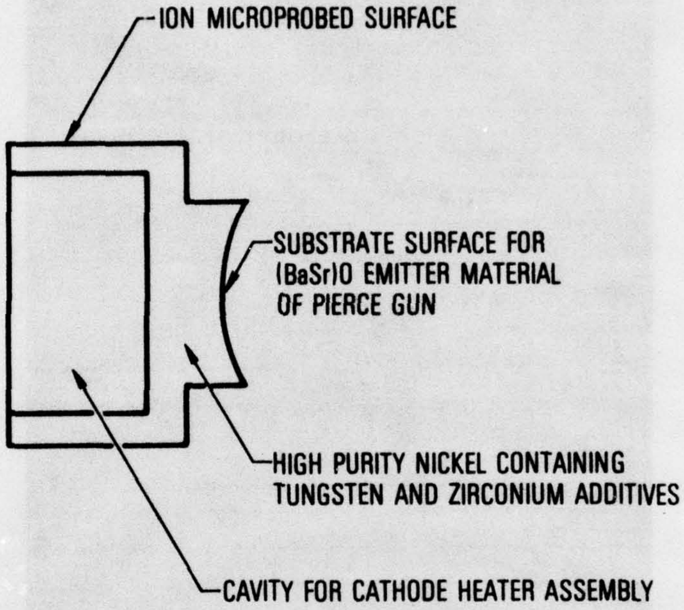


Fig. 3. Cross Section of a Typical Cathode Pellet

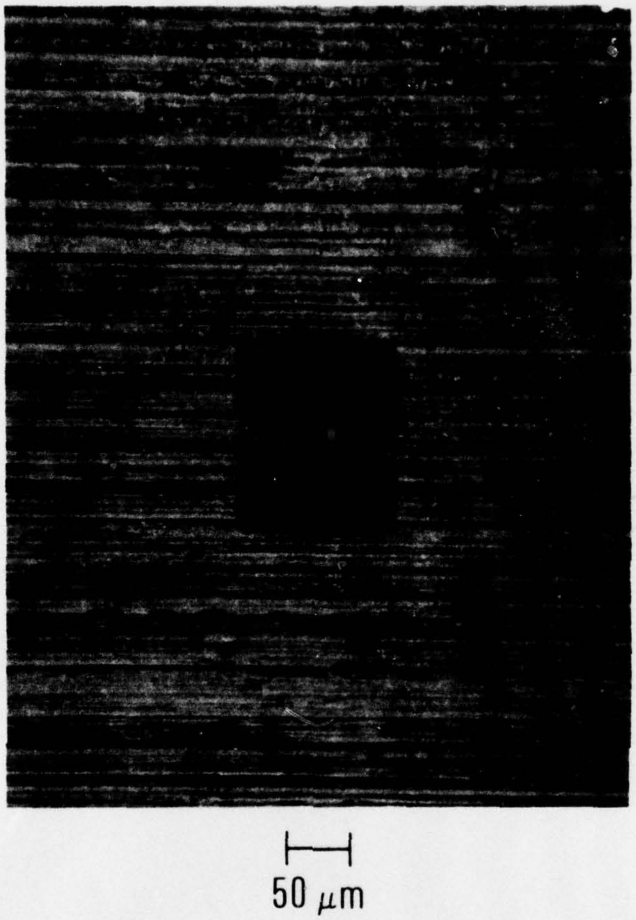


Fig. 4. Ion Microprobed Area on Surface of Cathode Pellet

that the bulk material below the surface is analyzed. The shape and size of the spot depend on the total ion beam current (10 nA in this case) and the cleanliness of the anode aperture of the duoplasmatron ion gun. The resulting mass spectrum is compared with that obtained via the raster mode to determine whether the latter spectrogram really represents the bulk composition of the nickel alloy.

Since contributions from the crater walls complicate the interpretation of the secondary ion yields produced via the point mode, only the data generated via the raster mode are used in the quantitative analysis for manganese. The measured $^{55}Mn^+$ and $^{90}Zr^+$ ion intensities are normalized to the measured $^{58}Ni^+$ ion intensity, and the manganese impurity content of the cathode nickel alloy is then deduced from the working curve (Fig. 5). If the manganese content of a cathode button is > 100 ppm, the pellet is ion-microprobed at another, adjacent location. If the result of this second analysis confirms the high manganese content of the cathode button, the IMMA is operated in the point mode with an $^{18}O_2^+$ beam current of 10 nA to ion-etch the entire length of the cylindrical surface. The combination of the two adjacent sputter-etched areas (roughly 280 × 112 μm) and the lengthwise ion-etched strip near the center provides unequivocal identification of the defective cathode pellet so that it may be disposed of.

The manganese content of the nickel alloys of Fig. 5 was determined by atomic absorption spectroscopy with an Instrumentation Laboratories spectrometer (Model 251). Air-acetylene flame atomization was used for manganese determinations. The composition of the solution that proved most

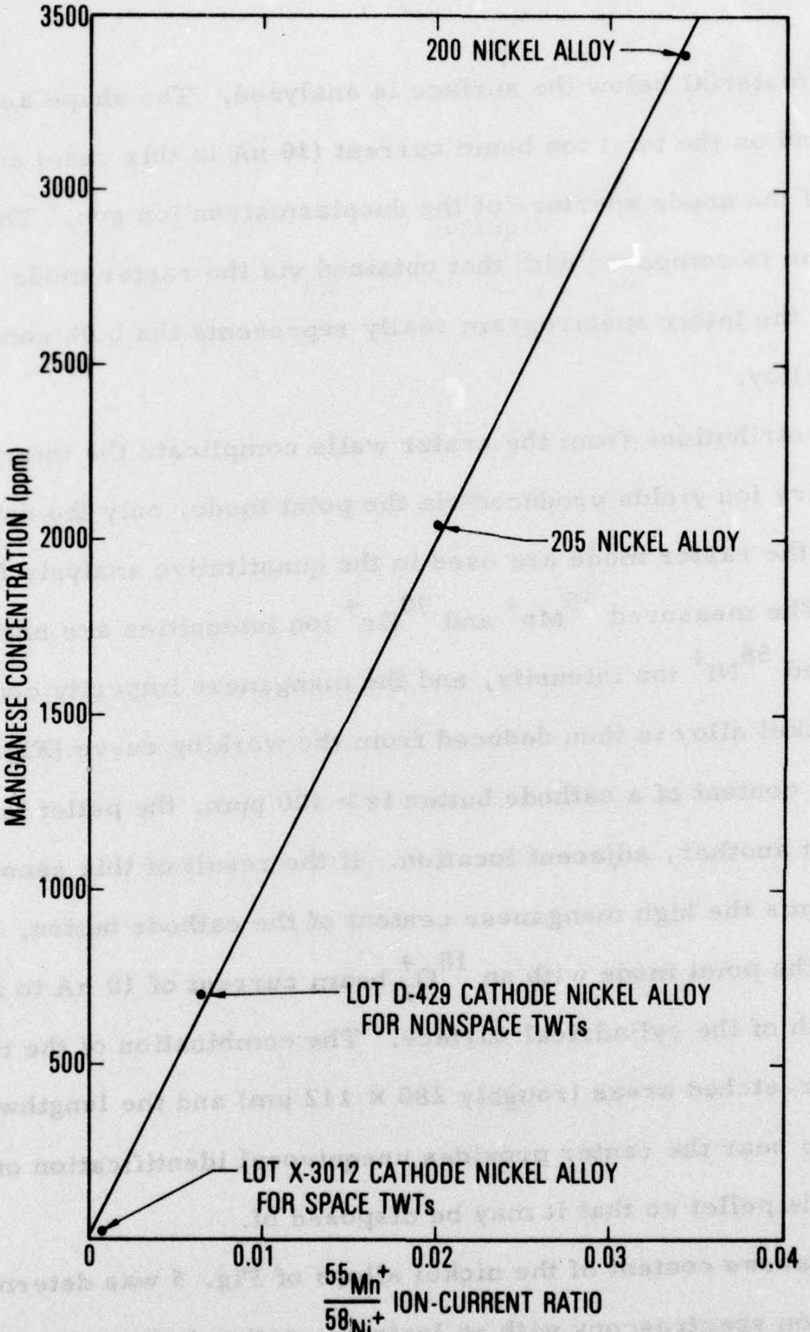


**Fig. 5. Manganese Working Curve**

successful for dissolving the nickel alloys was 54 percent nitric acid, 23 percent hydrochloric acid, and 23 percent deionized water. Depending on the sample size, the time required for complete dissolution varied from one to six hours. The high manganese content nickel alloys dissolved readily; whereas the ultrahigh purity 270 nickel, which contains less than 2 ppm manganese and is used to evaluate the effect of nickel concentration on the analytic technique for manganese, dissolved with great difficulty.

The cathode nickel alloys presented some additional problems because they contained $\sim$ 2 percent tungsten and $\sim$ 0.1 percent zirconium in addition to the manganese. On dissolution, these samples produced a bright lemon yellow precipitate that had to be removed by filtration. Subsequent IMMA analysis showed tungsten, zirconium, and a trace of nickel, but no manganese in the precipitate.

Calibration of the atomic absorption spectrometer was done using freshly prepared standards: 10, 1.0, 0.4, 0.2, 0.1, 0.05, and 0.01 ppm manganese. These standards were prepared by dissolving 99.99 percent pure manganese metal in hydrochloric acid to make a 1000-ppm solution of manganese and diluting it with 0.1M hydrochloric acid. Acid blanks were run for all samples, which without exception showed no absorption at the 279.5-nm manganese analytical line. Some nonatomic absorption was noted in the $>$ 10,000-ppm nickel solutions, but the background corrector of the instrument easily compensated for this interference.

## III. RESULTS

The effect of changing ionization efficiencies on in-depth analysis by ion sputtering mass spectrometry has been discussed by Storms [12]. He demonstrated that the sputtered ion intensities are not necessarily functions only of the corresponding elemental concentrations but are profoundly affected by the chemical nature of the bombarding ionic species due to surface chemical and kinetic effects, particularly within the first few hundred angstroms. These anomalous variations in the secondary ion yields have also been reported by other investigators [9], [10]. Based on the findings reported by Storms, a reactive electronegative molecular ion, $^{18}O_2^+$, was selected as the primary bombarding species to enhance and control the emission of sputtered ions. The $^{18}O_2^+$ rather than the $^{16}O_2^+$ molecular ion was chosen as the primary bombarding species to minimize interference with measurement of the secondary ion yields of the principal isotope of zirconium at m/e (mass-to-charge-ratio) = 90 amu by the ionic species $(^{58}Ni\,^{16}O_2)^+$ and of $^{55}Mn^+$ by $(^{12}C_3\,^{1}H_3\,^{16}O)^+$. When the surface of the nickel alloy is bombarded with $^{16}O_2^+$ ion, the ion-implanted content of $^{16}O$ atoms is sufficiently high to produce the undesirable $(^{58}Ni\,^{16}O_2)^+$ ion. Identification of the zirconium additive deliberately introduced into the cathode nickel alloy is imperative because zirconium is the principal activator that ensures that the barium-strontium oxide cathode will emit a steady and adequate supply of electrons for many years [15], [16]. Ultrapure 270 nickel, when bombarded with

$^{16}O_2^+$ ions, yields a secondary ion mass spectrum very nearly identical to that of a low manganese cathode nickel alloy. It is extremely difficult to differentiate these two spectra because the magnitude of the ion yields of the principal zirconium isotopes is not only small but varies considerably from spot to spot on the surface of a given cathode pellet. Ion image studies on the distribution of zirconium suggest that this beneficial additive is distributed nonuniformly and appears as agglomerates at the grain boundaries. Ultrapure nickel alone cannot provide the properties of long life expectancy and stability of electron emission that are required for oxide cathodes for space TWTs [17]. Since the focus electrode of the electron gun assembly is constructed from ultrapure 270 nickel, it is extremely important to establish unequivocally the presence of the zirconium additive in the cathode nickel alloy to differentiate between the two types of material and prevent cathode (eventually TWT) failures due to inadvertent material substitution. The detection limit of the IMMA for the secondary positive ions of the tungsten isotopes is inadequate to establish the composition of the cathode pellet as that of the double-additive cathode nickel. Approximately 2 percent tungsten is added to impart hot strength to the alloy and contribute some reducing element activity to ensure very long life cathode performance [17]-[19].

The sputtering rate of the nickel alloys has been ascertained by the usual interferometry technique to be ~ 13Å/sec when bombarded with 20-keV $^{18}O_2^+$ ions at a current density of 1 mA/cm$^2$. Thus, the five-minute ion sputter-etching of the surface removes material down to a depth of ~ 500Å below the machined surface and accomplishes two important functions. First, it removes most of the adsorbed surface-reacted oxygen and organic residues that produce the molecular ion $(^{12}C_3\,^{1}H_3\,^{16}O)^+$ with m/e = 55 amu, which interferes with the $^{55}Mn^+$ ion current measurement. Spectral interferences from $^{23}Na_2\,^{16}O_2^+$, $^{27}Al^{28}Si^+$, and $^{12}C_4\,^{1}H_7^+$ are minimal. Second, it prevents anomalous variations in the secondary ion yield of impurity atoms of interest as a function of depth during the subsequent quantitative analysis. Approximately three minutes are required to obtain an analytical mass spectrogram over the mass range from 1 to 150 amu. During this period, a layer of the nickel alloy material roughly a 100Å thick is sputtered away. The ion current data for $^{55}Mn^+$ and $^{58}Ni^+$ (Fig. 6) reveal no anomalous fluctuations in the secondary ion yield for these species due to a vicissitude in the implanted oxygen level as a function of depth. It may thus be concluded that the secondary ion yields obtained after the five-minute ion sputter-etching correspond to the elemental concentrations of a 100Å-thick layer of material roughly 500Å below the machined surface and are representative of the bulk concentrations.

The mass spectrograms of Figs. 7 and 8 are typical IMMA scans of cathode nickel alloys designated Z-8182 and X-3012, respectively. Cathodes made from these two lots of material have performed without exhibiting any appreciable degradation in cathode activity for more than five years in space TWTs and nearly a decade in TWT life tests. The cathode loading of these TWTs is about 200 mA/cm$^2$ at a cathode operating temperature of about 720° C.

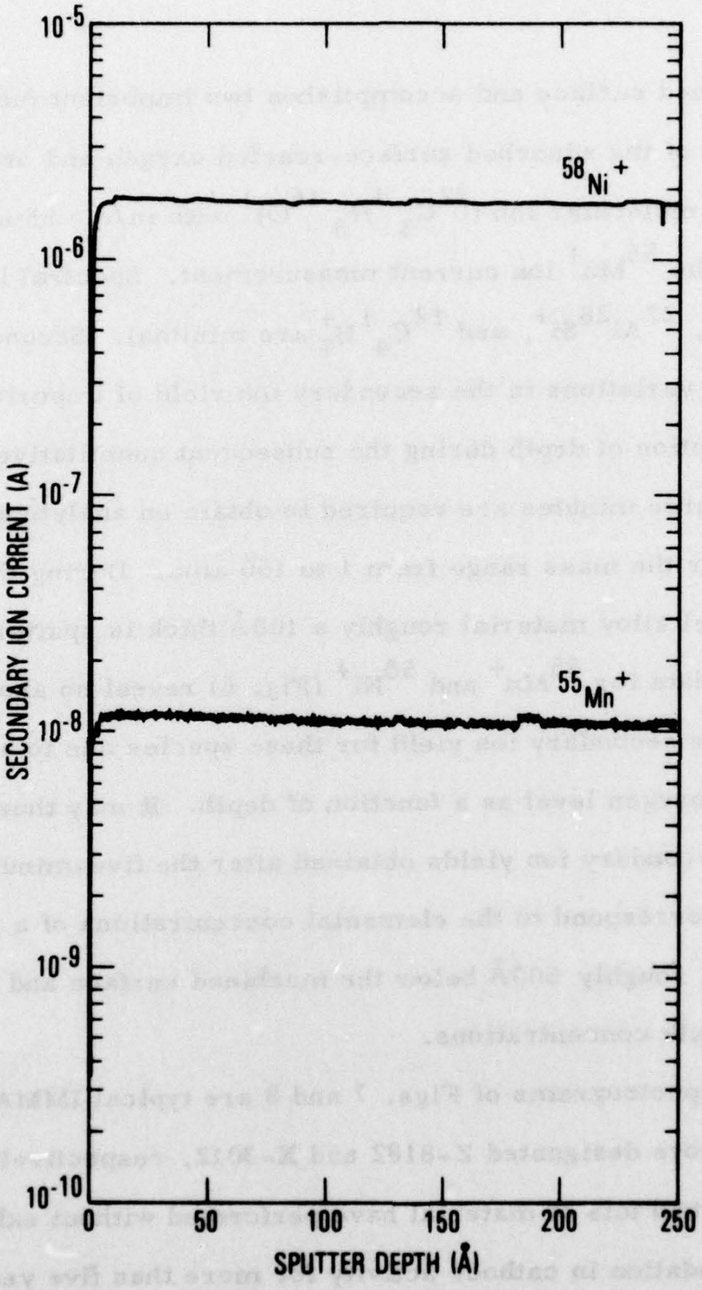


**Fig. 6. Sputtered Ion Intensities vs Sputter Depth in Nickel Alloy Used in Non-space TWT After Five-Minute Etch**

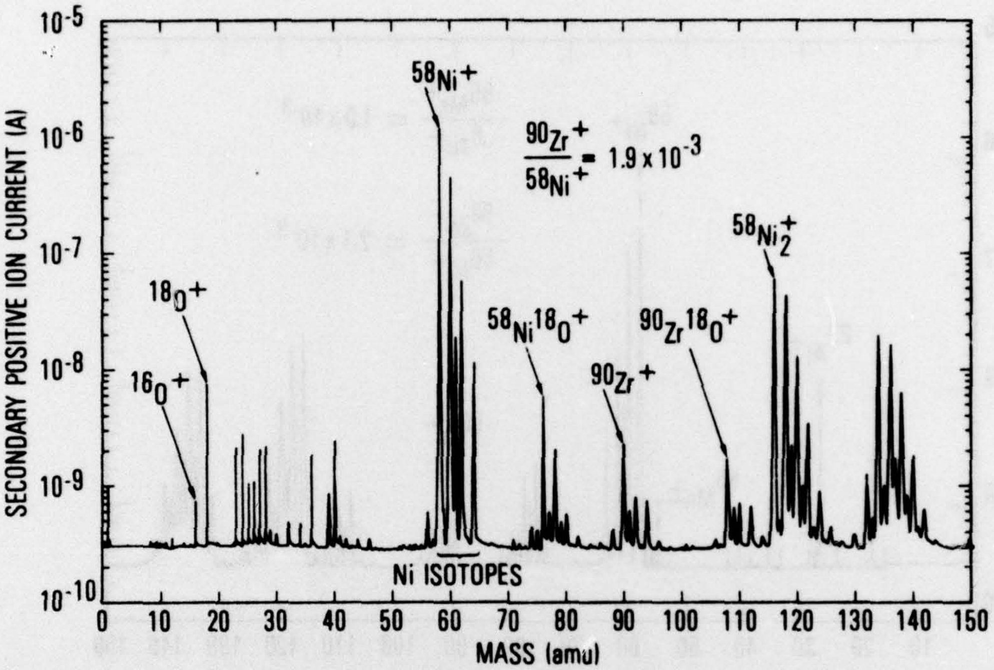


Fig. 7. IMMA Spectrogram of Z-8182 Cathode Nickel Alloy After Five-Minute Etch

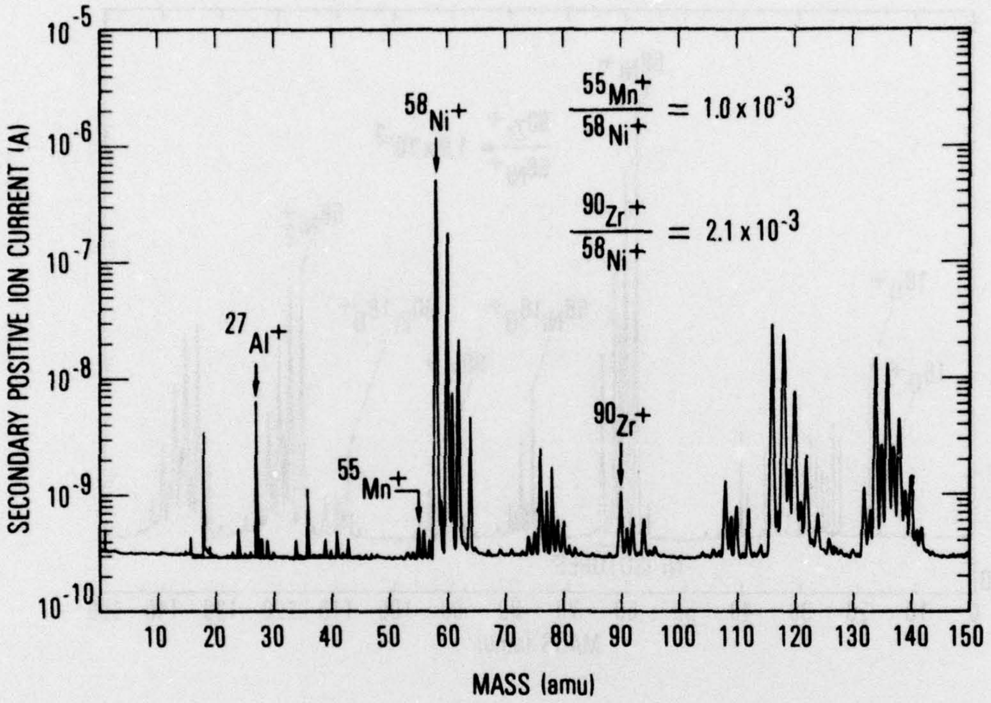


Fig. 8. IMMA Spectrogram of X-3012 Cathode Nickel Alloy After Five-Minute Etch

In contrast, a typical mass spectrum of a cathode nickel alloy identified as a D-429 lot of material is illustrated in Fig. 9. The results of failure analysis studies on defective TWTs that exhibited poor electron emission behavior, which is characteristic of short life expectancy oxide cathodes, revealed that the substrate of the barium-strontium oxide layer was fabricated from the D-429 double-additive nickel alloy. The details of this investigation will be published elsewhere. A comparison of the spectrograms shows that the D-429 material contains chromium and manganese. The manganese content deduced from the normalized $^{55}\mathrm{Mn}^{+}$ ion intensity ratio and the working curve of Fig. 5 is 650 ppm with an uncertainty of about 10 percent. The chromium concentration has been determined by atomic *absorption spectrometry to be 182 ± 40 ppm. Nitrous oxide-acetylene flame* atomization was used for the chromium determination.

Benjamin [20], in his comparative studies on the influence of substrate material on the thermionic electron emission of oxide cathodes, found that the 0.34 percent manganese-nickel base oxide cathode exhibited the worst electron emission characteristic in comparison with the 0.07 percent magnesium-nickel, 2 percent iron-nickel, 2 percent aluminum-nickel, and 0.2 percent thorium-nickel single-additive alloys. Poehler [21] also observed that the electron emission property of a 4.8 percent manganese-nickel base oxide cathode was considerably inferior to that of either pure nickel or 3.5 percent wolfram-nickel base oxide cathodes. These investigators attributed the impairment of electron emission to the development of a high

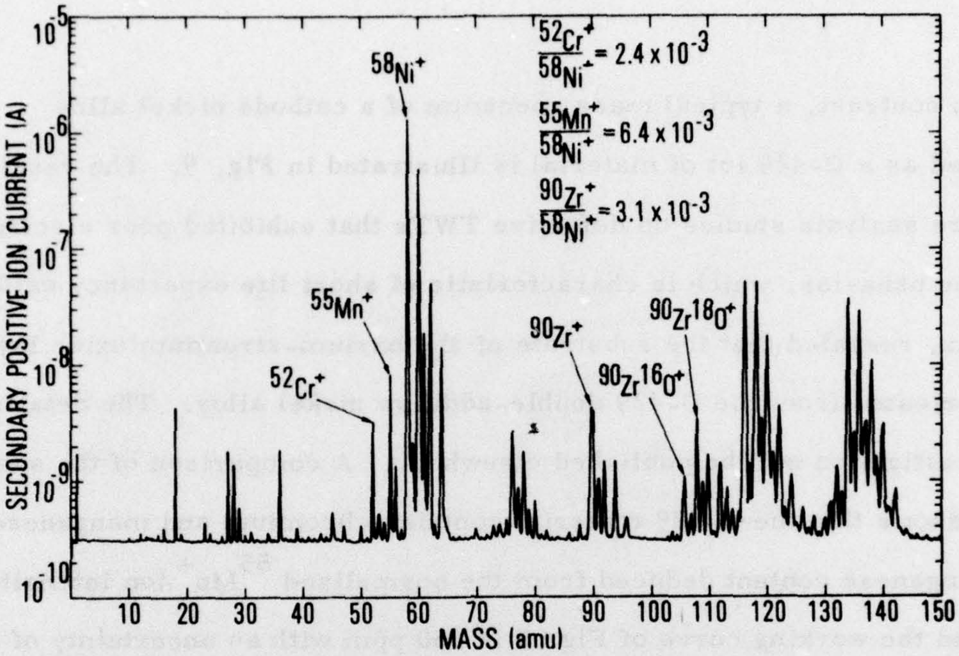


**Fig. 9. IMMA Spectrogram of D-429 Cathode Nickel Alloy After Five-Minute Etch**

impedance between the nickel alloy substrate and the barium-strontium oxide emitter material due to the formation of interface compounds of manganese. However, no evidence for the existence of interface compounds has been presented.

Fineman and Eisenstein [22] observed similar degraded electron emission characteristics from 5 percent chromium-nickel base oxide cathodes. They demonstrated that the degradation in cathode activity is accompanied by an increase in interface resistance and presented evidence for the existence of three possible interface compounds of chromium. It is not yet apparent that the recently observed impairment in cathode efficiency is the result of the formation of interface compounds because the impurity concentration levels are about two orders of magnitude less than that of the single-additive alloys studied by these investigators. Nevertheless, destructive failure analysis showed that every TWT with a certain type of degraded cathode activity that is manifested by a short-lived oxide cathode, without exception, contained a D-429 type of cathode nickel alloy. A correlation coefficient of unity strongly suggests that the D-429 lot of material is somehow responsible for the observed phenomenon in the defective TWTs and that it should not be used as the substrate for the oxide cathodes in high reliability, long-life TWTs for space applications.

Although the ion microprobe technique is destructive, i.e., material is consumed in the sputtering process, the damage resulting from the sputtering (Fig. 4) is less than some of the defects on the surface introduced by the machining process. The crater formed by the point mode of analysis is about 25 μm in depth and 25 μm in diameter. The miniscule amount of material consumed has not been found to jeopardize the performance of the double-additive nickel alloy as a substrate for the barium-strontium oxide emitter material. Thus, from a practical standpoint the technique described may be viewed as nondestructive.

# IV. CONCLUSIONS

Several different commercially available nickel alloys (types 270, 220, 205, and 200) and other double-additive (wolfram and zirconium) cathode nickel alloys are used in the fabrication of the electron gun assemblies of TWTs for both space and nonspace applications. Most of the 200 series of nickel alloys contain small quantities of manganese (< 0.35 percent). Controlled amounts of manganese are added to the nickel alloys as a "deoxidizing" or "degassifying" agent to prevent bubble formation during the casting operation and as a getter for residual sulfur to improve the high-temperature malleability of the alloy [18]. Hence it is prudent to verify the composition of the cathode nickel alloy to prevent premature TWT failures in spacecraft resulting from inadvertent material substitution or from the use of cathode nickel alloys with essentially the same elemental composition and concentration levels of detrimental impurities as those of the D-429 type of material. The IMMA technique described here is ideally suited for use as a standard quality assurance/quality control procedure for accomplishing this objective. It is nondestructive, does not jeopardize the subsequent performance characteristics of the nickel alloy as a substrate for the barium-strontium oxide cathode, and is capable of differentiating among the different nickel alloys.

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