GAS EVOLUTION VERSUS TIME

FROM PLATED LIDS VIA MASS SPEC

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GOLD PLATED LID GAS EVOLUTION ANALYSIS VERSUS TIME

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The problem of moisture in ceramic packages sealed with gold (Au) plated metal lids and gold - tin (AuSn) solder has been ascribed, at least partially, to the reaction of oxygen from variously attributed sources with hydrogen (H2) that is evolved from the lid plating. This has been concluded from residual gas analysis (RGA) done on sealed packages and from fusion analysis for H2 contained in the lids. It was felt that this data has not been sufficient to indicate exactly what is evolved from plated lids during the sealing operation. RGA data always shows CO and CO2 in appreciable quantities as well as H2O and often H2.

It was decided to isolate the lid from the rest of the system and attempt to determine what species are evolved during heating of this component alone.

EXPERIMENTAL METHOD:

Mass spectrometry was applied using a Quadrex 100 Residual Gas Analyzer, manufactured by Leybold -Inficon. The software as furnished with the equipment has been modified extensively. The system performs consecutive analyses at a rate of 2 to 3 per second. It has channels for atomic mass units (AMUs) from 1 to 100. Accumulative data storage, however, can only be done on 7 channels at a time - one for total chamber pressure and six AMU

choices. Data pints were stored every 30 seconds only, due to computer interface restrictions. Since all experimental runs were from 20 to 80 minutes, this accumulation rate is sufficient.

Test samples consisted of 50 gram lots of plated lids. Base metal was either Kovar (FeNiCo) or Alloy 42 (58Fe 42Ni) 0.010" (0.25mm) thick plated with an average of 165 microinches (4.2 microns) of Ni and an average 65 microinches (1.8 microns) of Au. Resultant total surface area was about 70 in2 (452 cm2). The sample was contained in a quartz tube with an ID of 0.59" (15 mm) and a length of 15 " (38.1 cm). The tube was connected via Tygon vacuum tubing to the valving system on the Quadrex unit.

Each sample was evacuated to 1 E-5 Torr at which point the mass spec sampling chamber was opened and data recording begun. Data was accumulated for 3 minutes at room temperature. The sample tube was then inserted into a preheated furnace at the chosen temperature and sampling and recording continued until species evolution ceased or it was concluded that nothing was occurring.

The object of the experiments was to determine what species are evolved and to attempt to determine their source in the manufacturing operation. Consequently no effort was made to develop quantitative data. Some samples were analyzed for H2 content before and after RGA runs - by LECO Corporation, St. Joseph, Michigan.

INITIAL PROCEDURES AND RESULTS:

An initial testing temperature of 500 C was chosen. Previous H2 fusion analyses had demonstrated that heating at this temperature for reasonable periods of time (1 hour or less) resulted in reduction of H2 contents to base metal levels whereas lower temperatures did not. Testing was also done at 360C to simulate maximum package sealing temperatures. (Figure 6 is a comparison of H2 evolution curves at the two temperatures. It clearly demonstrates the much more rapid and complete evolution of this specie at the higher temperature, and will be further discussed later.)

The first mass spec runs were made monitoring the full range of available AMUs. Peaks were seen at AMU 2, 16, 17, 18, 28, and 44. It is assumed that these AMUs correspond to H2, CH4, OH, H2O, CO/N2 and CO2, which are the expected species or derivatives as seen in RGA data from sealed packages. All of these peaks steadily decreased over time except AMU 2, which increased. Initially, they were chosen as the channels to monitor in the accumulative storage mode.

It was quickly determined that the only channel which showed detectable increases in pressure was AMU 2. All others followed the same curve as the system pressure. Figure 1 shows curves for AMU 2 for two different plating lots. Lot 16167-1 was a standard lot. 16167-2 was plated in a manner purposely designed to increase H2 content. Included with the figure is LECO data on total H2 content as plated and after the mass spec

runs. The after run numbers of 0.39 and 0.40 ppm are consistent with much previous data on bare Alloy 42, indicating that all H2 originating from the plating has been removed.

Figure 2 shows the AMU 18 curves from the same runs, demonstrating that there was no evolution of H2O from the parts. This is concluded by comparing Figure 2 to Figure 3 which shows the total chamber pressure during the runs.

FURTHER PROCEDURES AND RESULTS:

Having demonstrated that the important species is H2, it then became desirable to attempt to find the source/sources of H2 in the manufacturing procedure. Two sets of samples were prepared for this purpose.

The first set, from plating lot 59230, consisted of five samples which were removed after each step of the plating operation. Ie; (1) bare Kovar lids, (2) plated with a Ni strike, (3) Ni strike + Ni plate, (4) Ni strike + Ni Plate + Au strike, and (5) Ni strike + Ni Plate + Au strike + Au plate.

The second set, from plating lot 16167, consisted of five samples run only in each of the plating steps. Ie; (1) bare Kovar lids, (2) Kovar plated with Ni strike only, (3) Kovar plated with Ni Plate only, (4) Kovar plated with Au strike only, (5) Kovar plated with Au plate only.

Figure 4 contains the AMU 2 (H2) plots from running the five samples of the first set, each at 500C, but for varying lengths of time. Each run was terminated only after H2 evolution appeared to cease, except for the Ni strike sample which was

arbitrarily stopped after reaching a low plateau. Figure 5 contains the AMU 18 (H2O) plots for the same runs.

Figure 8 contains the H2 plots from the five samples of the second set. Figure 9 contains the H2O plots and Figure 10 contains the chamber pressure plots from the same runs. The data in these three figures was started just before the mass spec sampling valve was opened, so the first data points represent chamber blank off values.

There are two "down spikes" in the Ni strike curves in both data sets. These were caused by temporarily closing the sampling tube valve to check background values. They do not represent actual changes in H2 evolution.

It is obvious from Figures 4 & 8 that the major sources of H2 are the Ni plate and the Au strike, with the Ni strike and final Au plate contributing a relatively minor amount.

The isolated Au plate curve (in Figure 8) shows no real evolution until after 10 minutes at heat, and then rises to a much lower level than the Ni plate and Au strike. Overall H2 evolution, as seen in Figures 1 and 6 and as the Au Plate plot in Figure 4, is really from the Ni plate and Au strike layers and is controlled by diffusion through the main Au layer.

This is further confirmed by the actual H2 evolution data listed on Figure 6. H2 evolution was complete after about 50 minutes in 500C (2.07 - 0.46 = 1.61 ppm) and was still well in progress after 70 minutes in 360C (2.07 - 1.41 = 0.66 ppm).

POTASSIUM CYANIDE EVOLUTION:

As the above tests were being run, it was obvious that we were seeing nothing on the other channels we were measuring, so the channels were changed from run to run to explore the possibility of other evolved species. AMUs 35 (Cl) and 32 (O2/S) showed no peaks. AMU 39 (K) showed up on a 500C run as very erratic but steadily increasing data points. This is the run represented in Figure 6. As a consequence, the next run, which was the 360C run in Figure 6, was set to monitor AMUs 26 (CN) and 52 (C2N2). Figure 11 shows the AMU 39 curves for both runs. Figure 12 shows the 39 and 26 curves for the 360C run. AMU 52 showed several spikes above zero after 50 minutes. We have no explanation for this steady increase in probable KCN evolution but the data has been confirmed and is consistent.

CONCLUSIONS:

(1) H2 is far and away the primary evolved specie during heating of Au and Ni plated metal lids.

(2) The major sources of H2 are the Ni Plate and Au strike.

(3) The rate of evolution is temperature dependant and is quite low and slow at normal package sealing temperatures.

(4) A method has been developed for qualitatively evaluating evolved species resulting from heating plated lids. The results are still limited and a great deal of work remains to be done.

Hydrogen Evolution at 500C,
Two Standard Plating Runs.

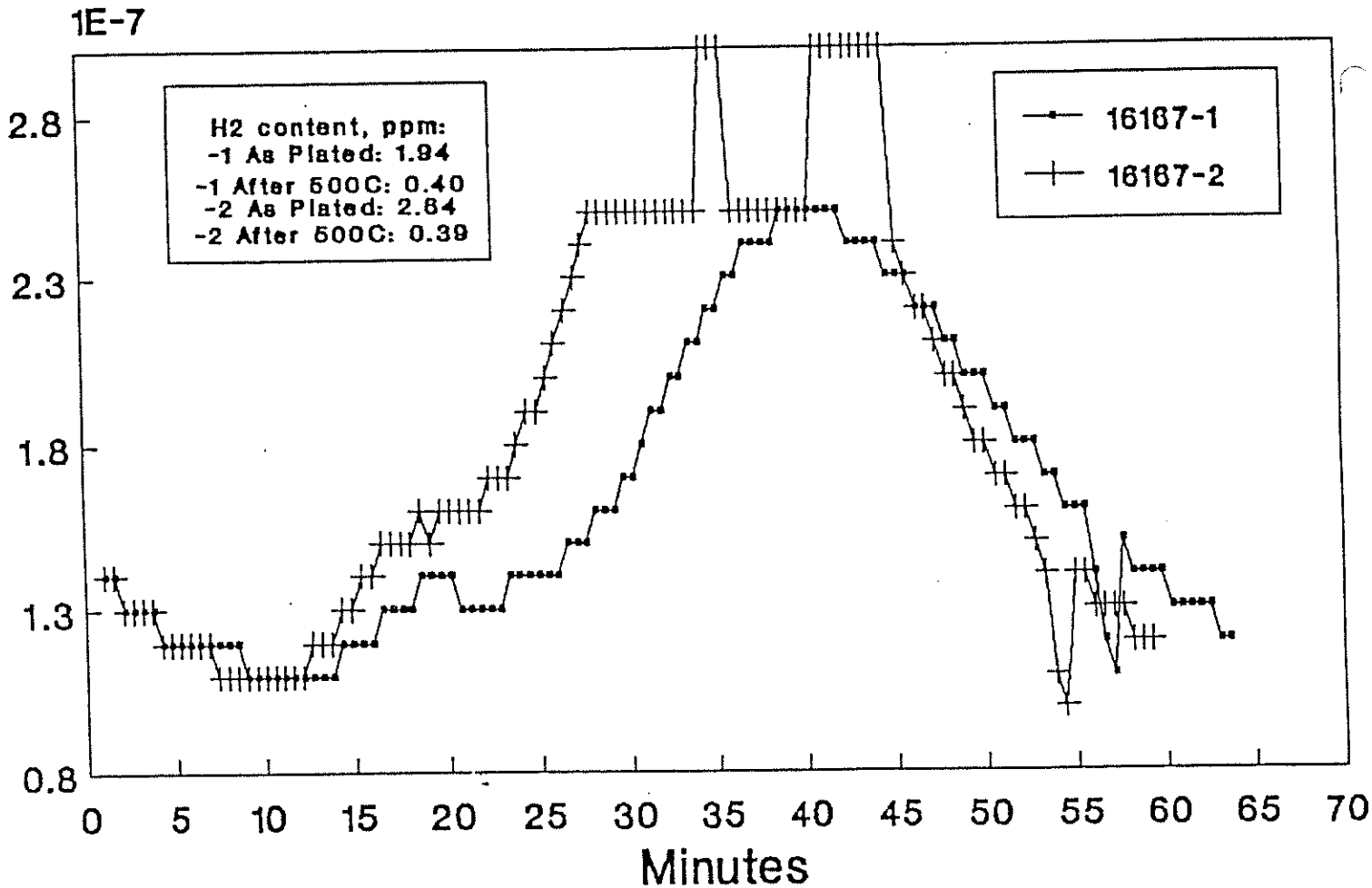

FIGURE 1

Water Evolution at 500C.
Two Standard Plating Runs.

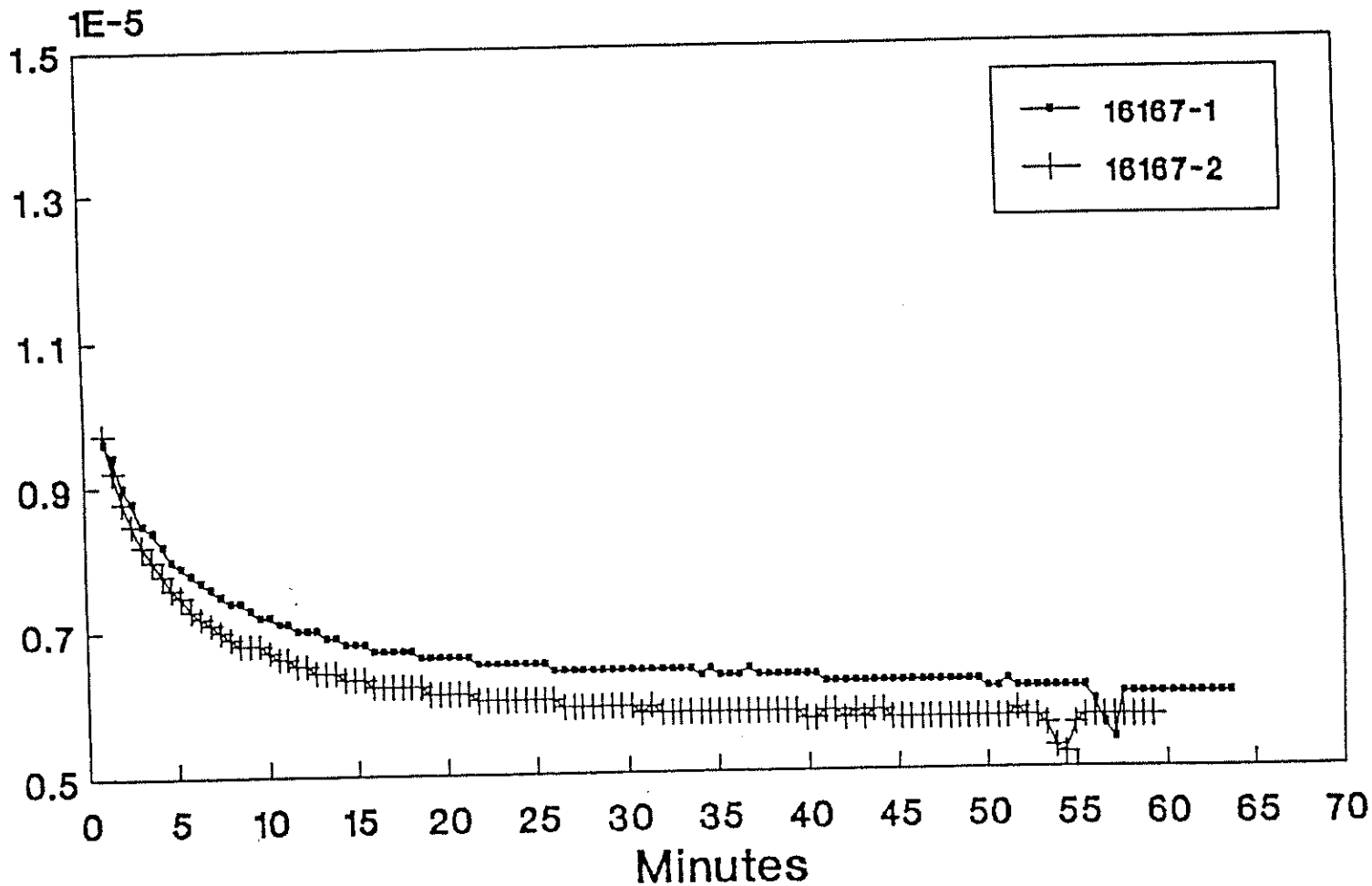

FIGURE 2

Analysis Chamber Pressure,
Two Standard Plating Runs.

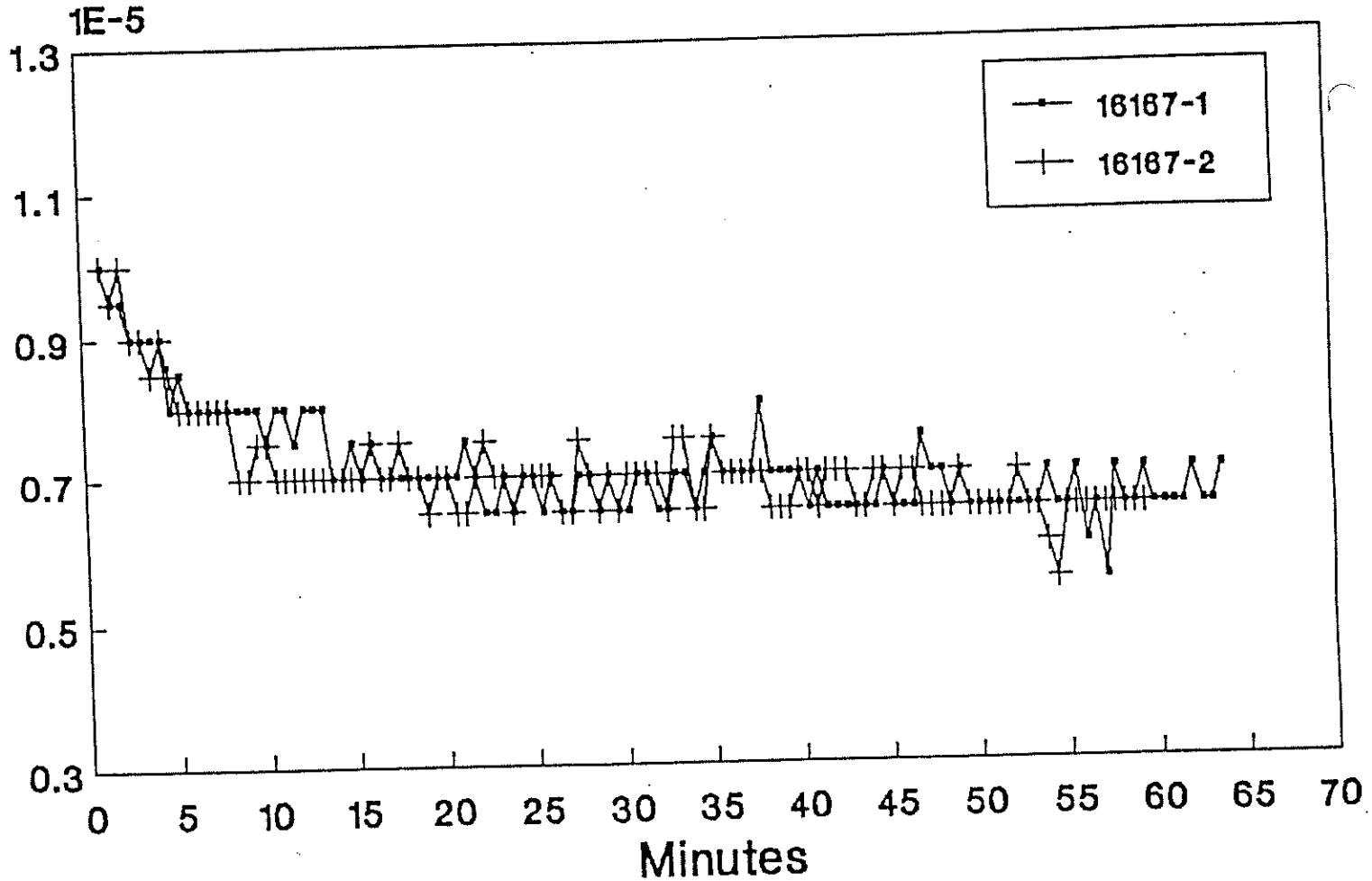

FIGURE 3

Hydrogen Evolution at 500C, lot 59230.
Measured After Each Plating Step.

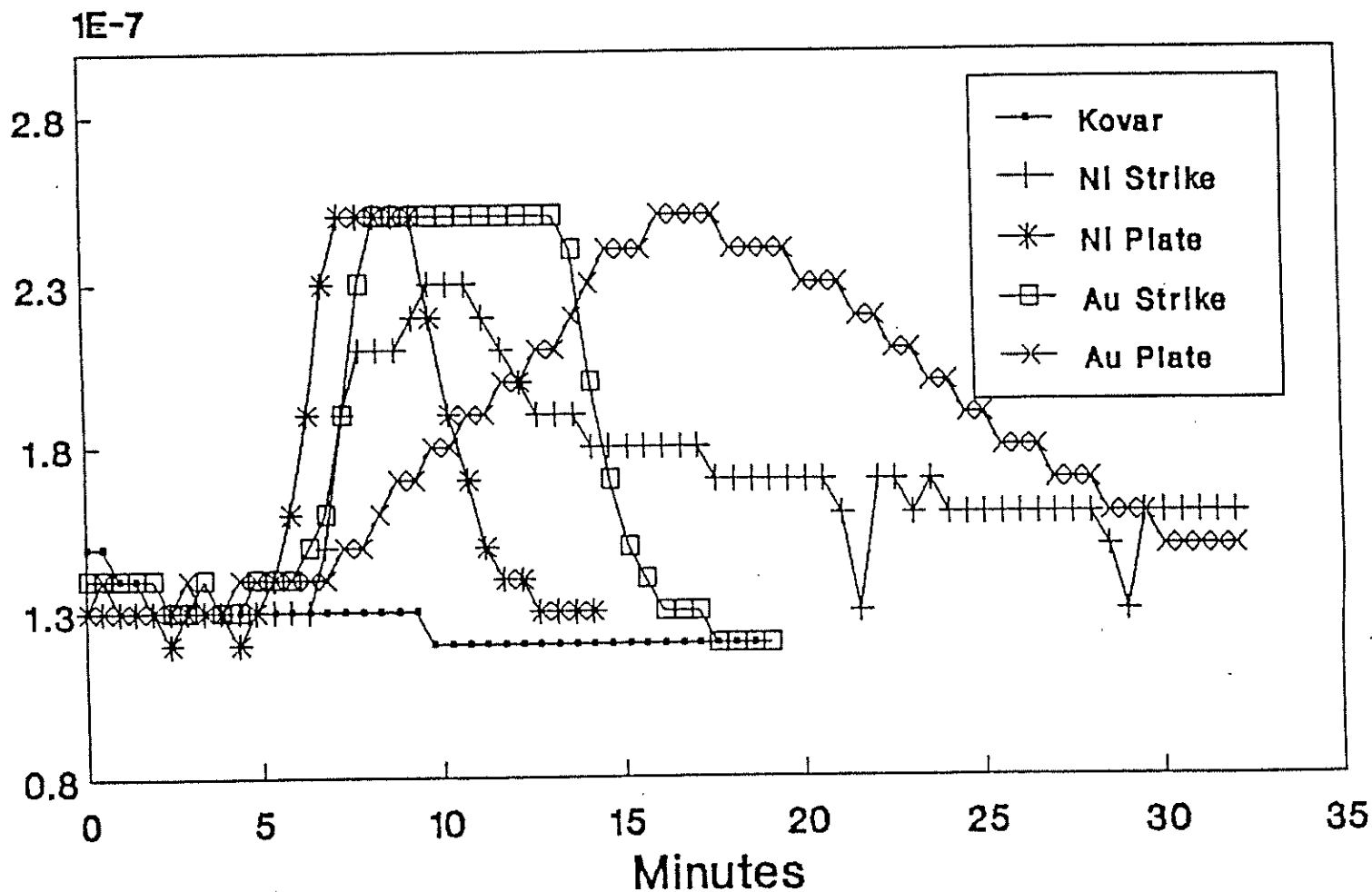

FIGURE 4

Water Evolution at 500C, lot 59230.
Measured After Each Plating Step.

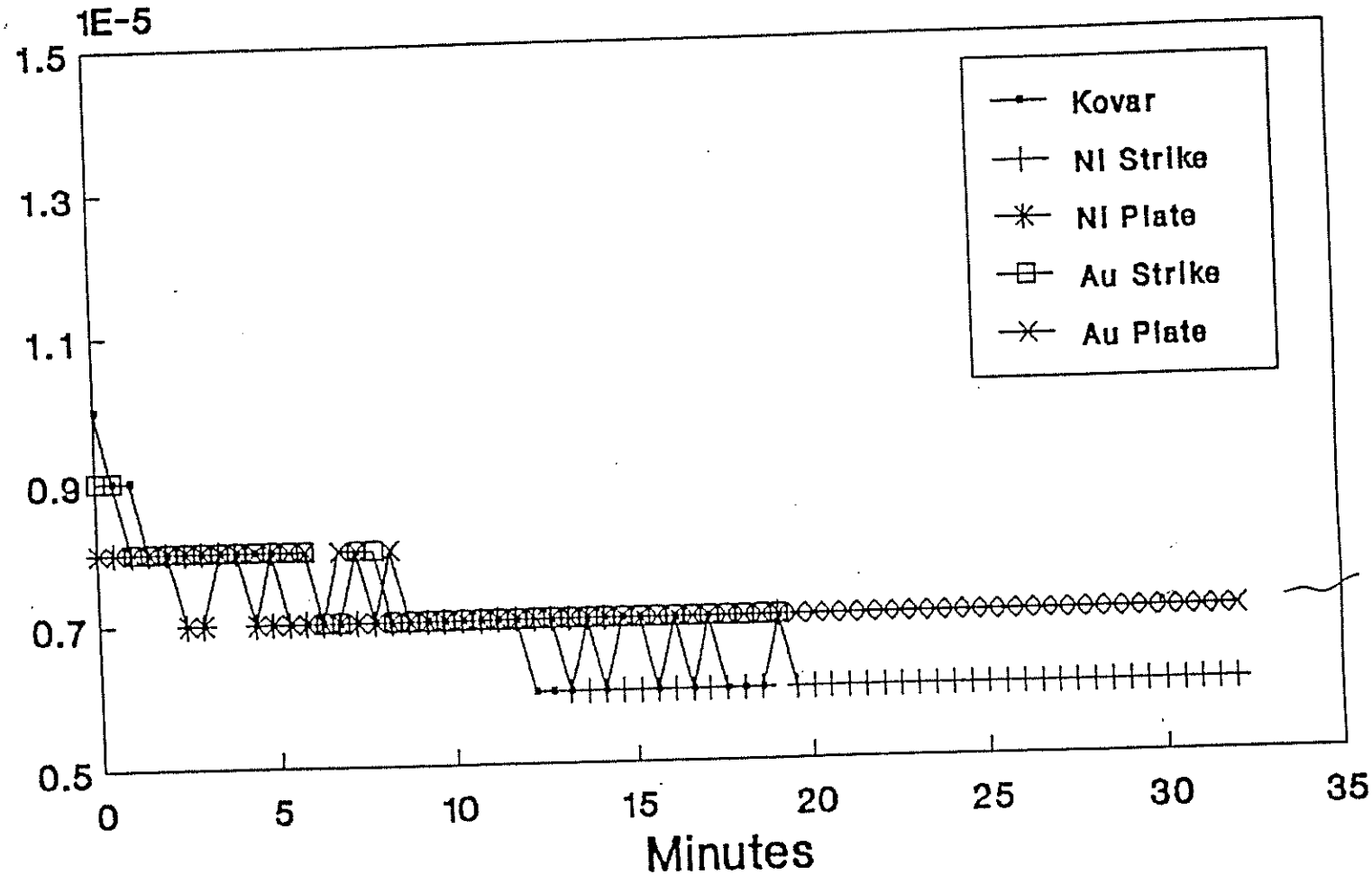

FIGURE 5

Hydrogen Evolution at 360C and 500C.
Standard Plated Lids, lot 60980.

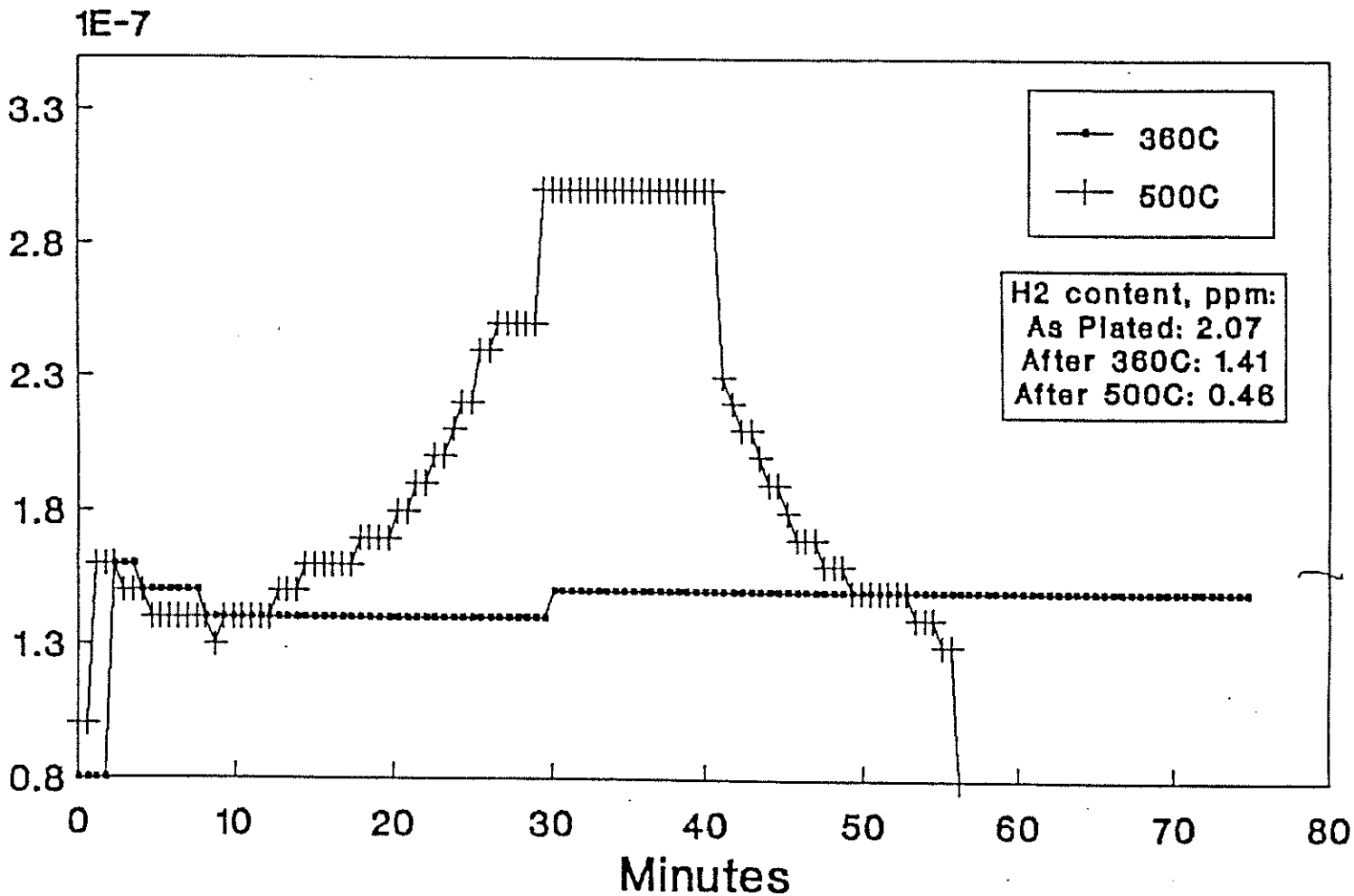

FIGURE 6

Water Evolution at 360C and 500C.
Standard Plated Lids, lot 60980.

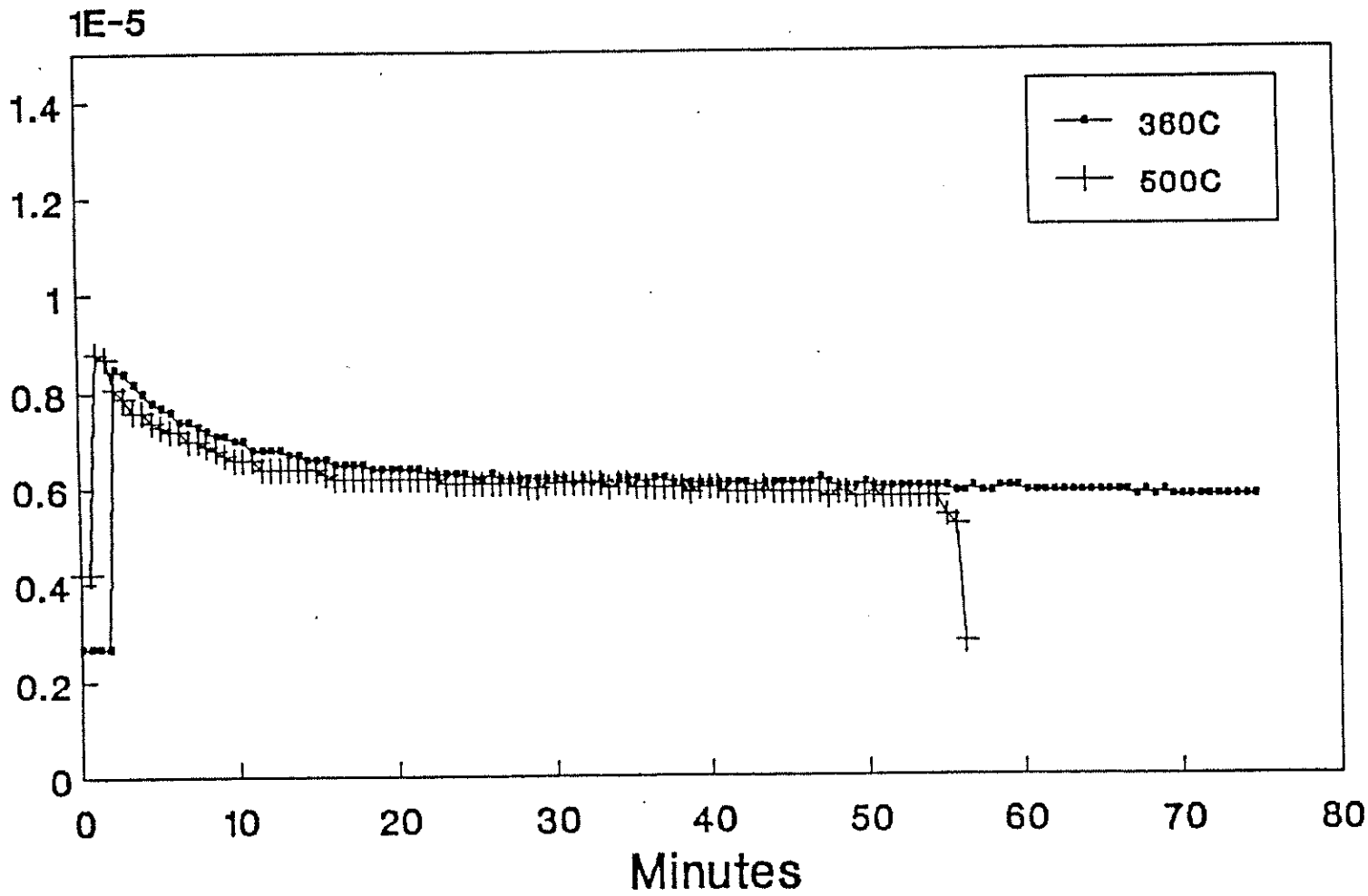

FIGURE 7

Hydrogen Evolution at 500C, lot 16167.
Isolated Plating Steps.

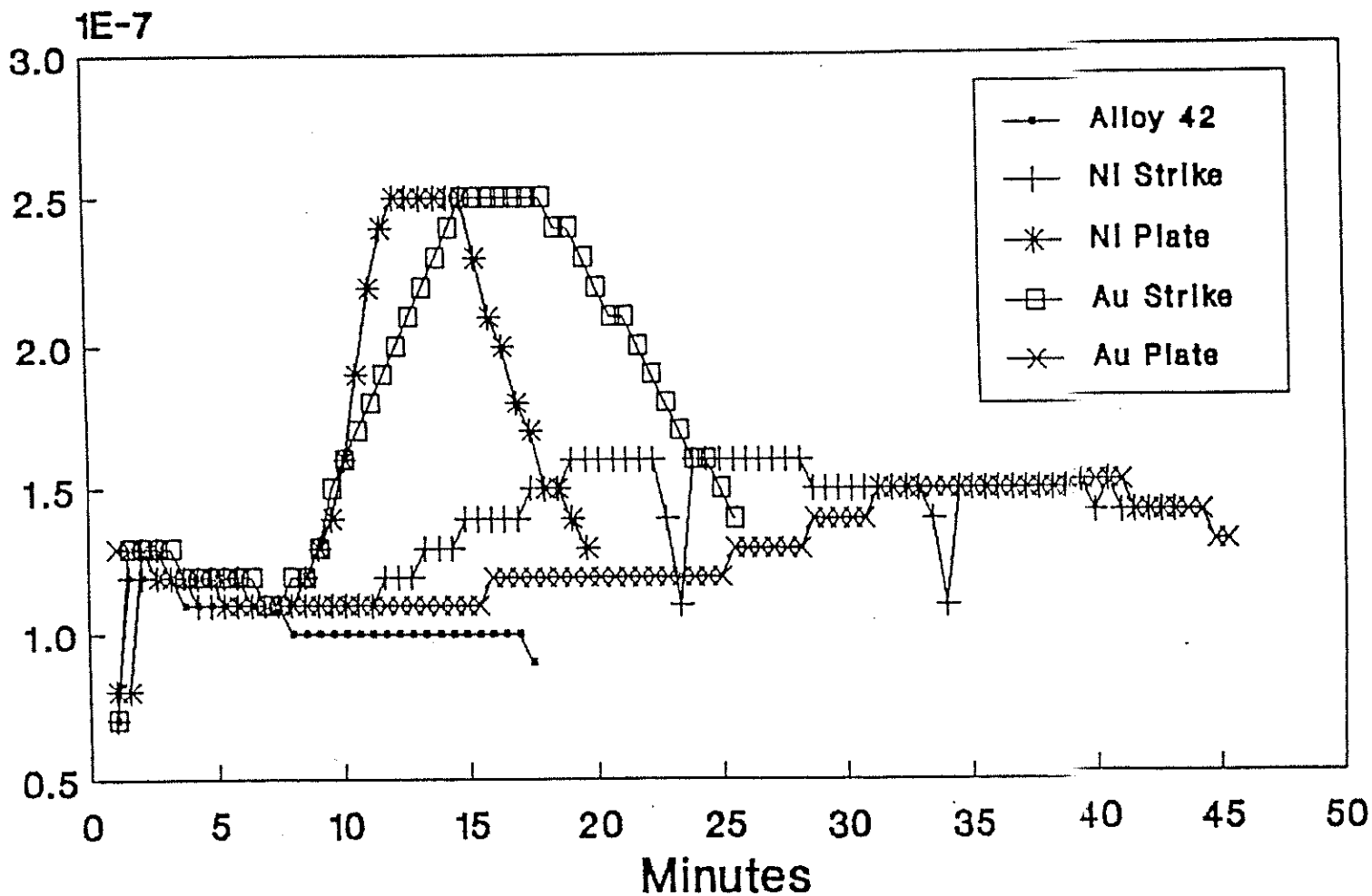

FIGURE 8

Water Evolution at 500C, lot 16167.
Isolated Plating Steps.

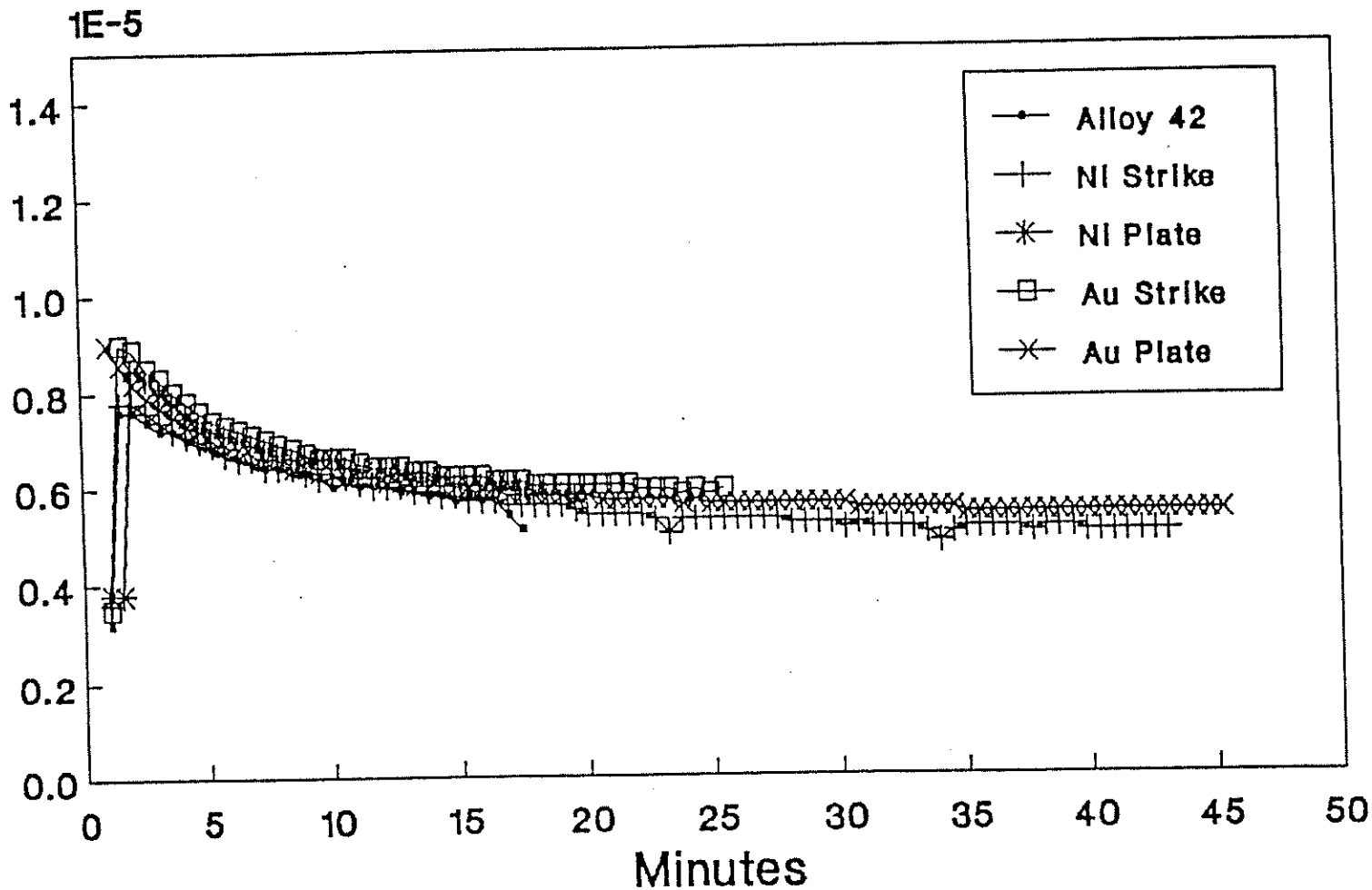

FIGURE 9

Analysis Chamber Pressure, lot 16167.
Isolated Plating Steps.

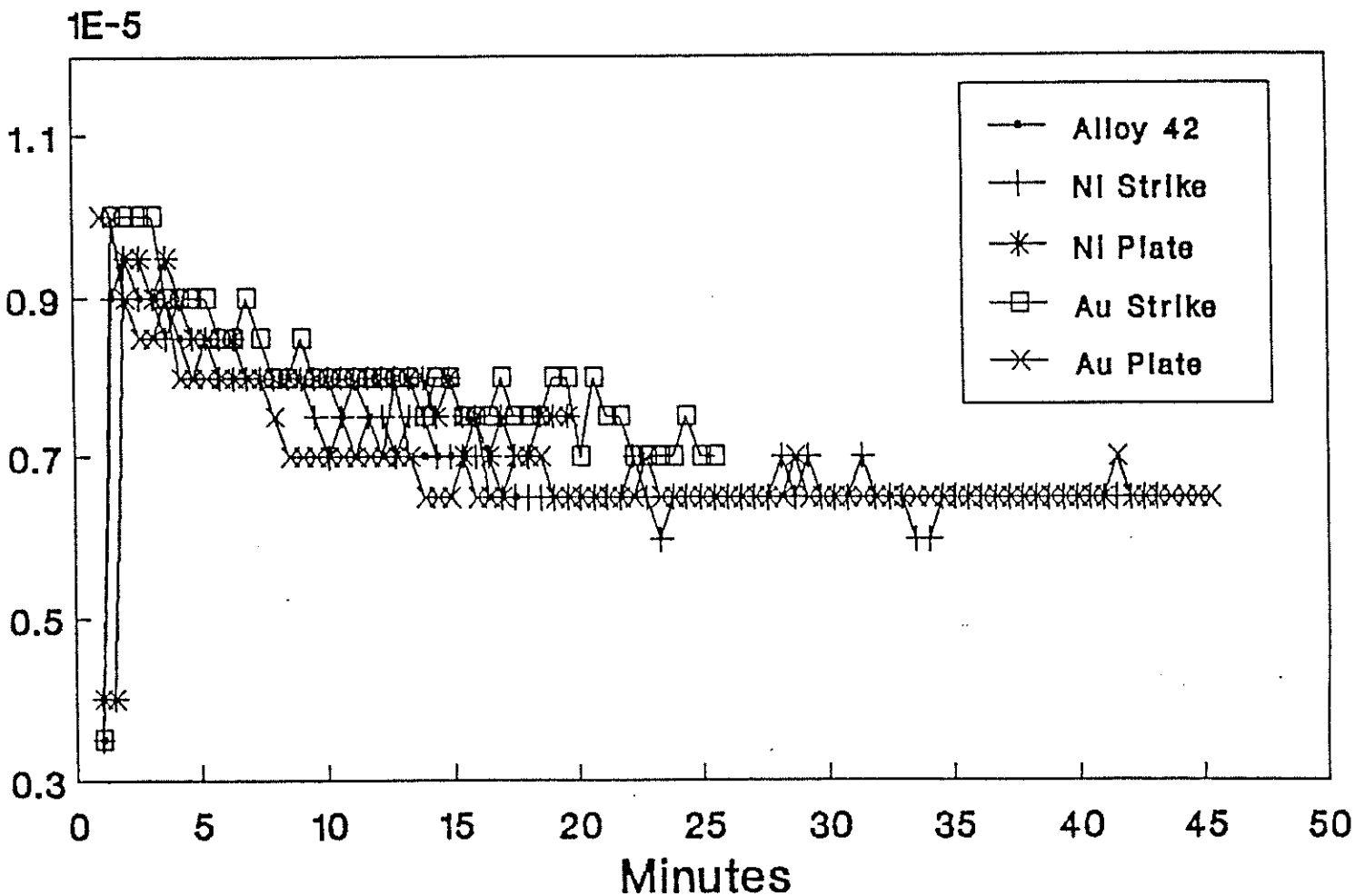

FIGURE 10

Potassium Evolution at 360C and 500C.
Standard Plated Lids, lot 60980.

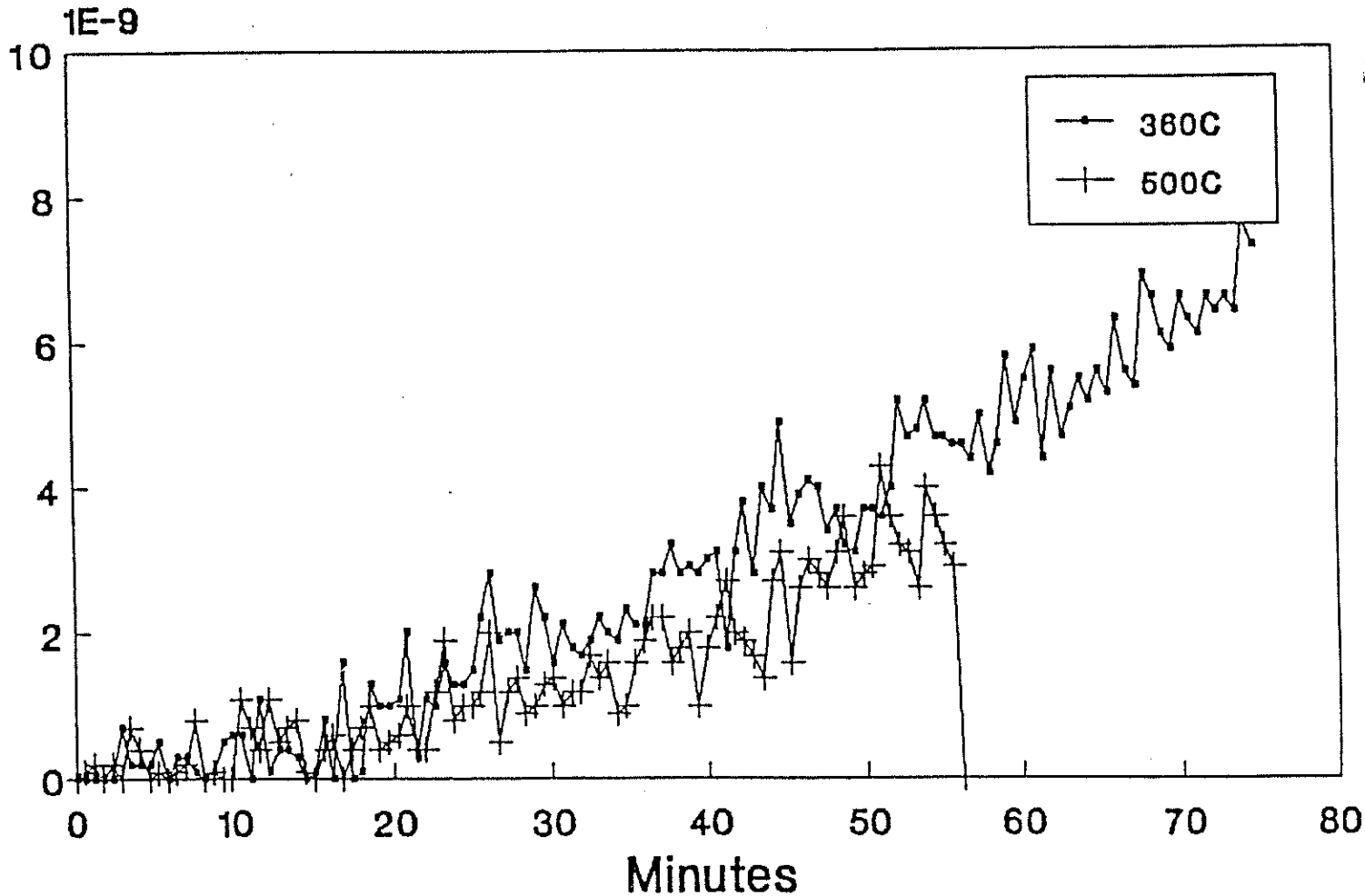

FIGURE 11

Potassium Cyanide Evolution at 360C.
Standard Plated Lids, lot 60980.

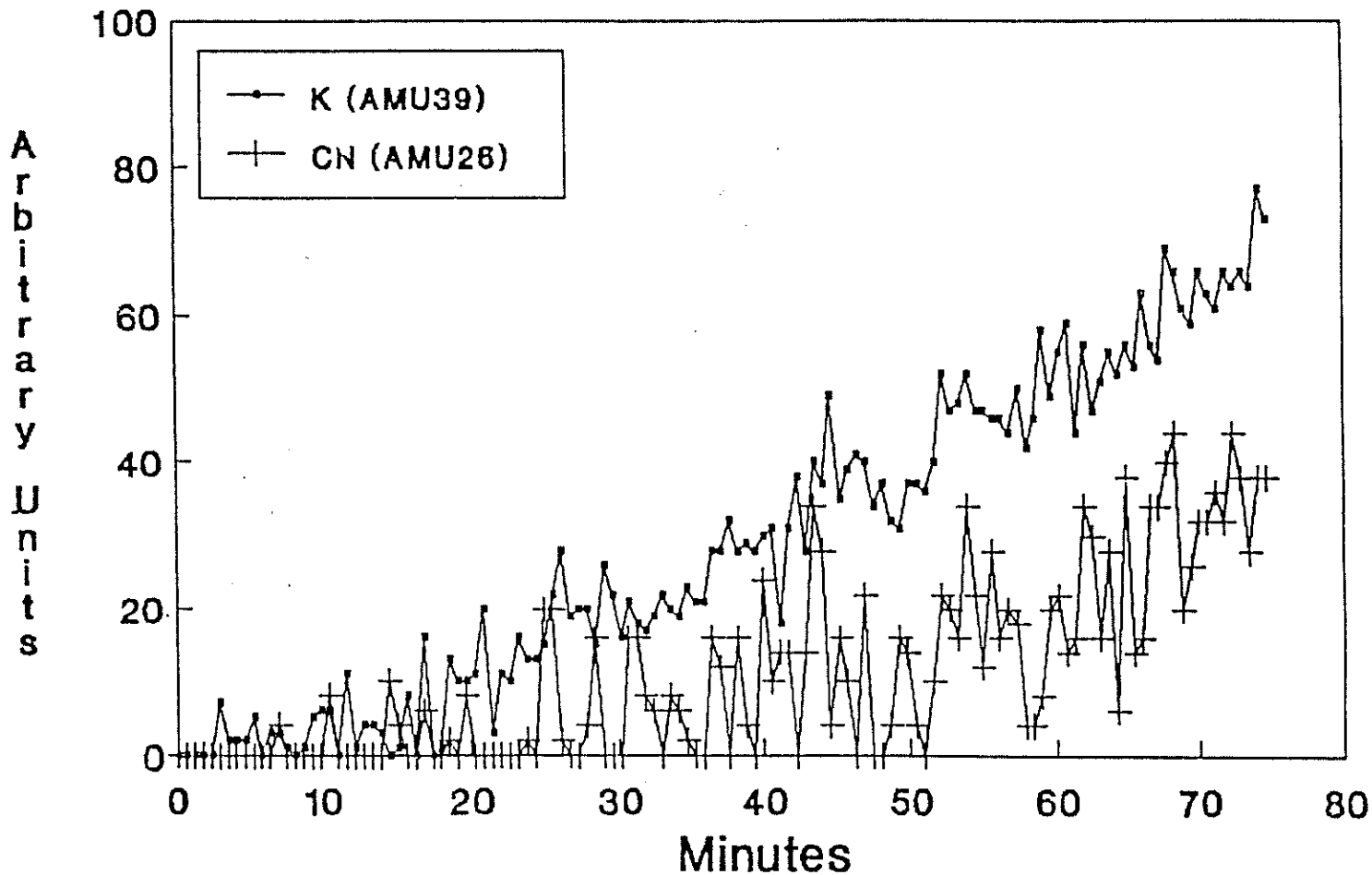

FIGURE 12