

THE SMOKE-ION SOURCE: THE GENERATION OF METAL AND METAL OXIDE
CLUSTER IONS VIA INERT GAS CONDENSATION

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RECENT PUBLICATIONS, SUBMITTAL FOR PUBLICATION AND PRESENTATION:

- A) K.M. McHugh, H.W. Sarkas, J.G. Eaton, C.R. Westgate, and K.H. Bowen, "The Smoke Ion Source: A Device for the Generation of Cluster Ions via Inert Gas Condensation" Z. Phys D-Atoms Molecules and Clusters, 12, 3 (1989).
- B) K.H. Bowen, presented at the "Workshop on Structural and Electronic Properties of Systems with Reduced Size and Dimensions," Virginia Commonwealth University, Richmond, Virginia, May, 1990.
- C) K.H. Bowen, in "An Evaluative Program for Assessing the Utility of Cluster Ions in Semiconductor Processing," Report to the Semiconductor Research Corporation, 1990.
- D) K.H. Bowen, presented at the "5th International Symposium on Small Particles and Inorganic Clusters," Konstanz, Germany, Septemeber, 1990.

ABSTRACT

We report on the further development and mass spectrometric characterization of our Smoke-Ion Source. This ion source is capable of generating intense, continuous beams of both positive and negative cluster ions of metals, metal oxides, and other relatively high temperature materials. This device is the result of the marriage of the inert gas condensation method for generating metal smokes with techniques for injecting electrons directly into expanding jets. Intense cluster ion beams have been generated from metal smokes of lead, lithium, sodium, magnesium, and from mixed lithium-magnesium smokes. In addition, metal oxide cluster ions of lithium and of magnesium have also been generated. Future studies will focus on mass spectral studies involving new materials and on probing, via negative ion photoelectron spectroscopy and photoabsorption experiments, the electronic energy levels of size-selected cluster ions generated with this source .

BACKGROUND

We report on the continuing development and characterization of a source for generating intense, continuous beams of metal and metal oxide cluster ions. This device¹ is the result of combining the inert gas condensation method with techniques for injecting electrons directly into expanding jets. Inert gas condensation is a proven approach for generating strong beams of large neutral clusters comprised of relatively high temperature materials.²⁻⁹ In inert gas condensation cells, an oven evaporates the material of interest into a bath of cool inert gas. The evaporated material supersaturates in this cool environment and nucleates to form a dilute smoke composed of ultrafine particles and clusters. The inert gas, along with its entrained smoke, then exits the cell through a small aperture into a high vacuum region where it forms a beam. The injection of low energy electrons directly into the high density region of supersonic expansions has been shown to be a highly efficient method for generating beams of both positive and negative cluster ions.¹⁰⁻¹²

Several investigators had previously generated positive cluster ions from inert gas condensation cells, usually in the course of mass spectrometric characterization studies. In each case, this was accomplished well downstream of the cells' exit apertures by subjecting the neutral cluster beams to either electron bombardment ionization or to photoionization.⁴⁻⁹ In the present work however, electrons from a biased filament are injected in a close-coupled manner directly into the weak jet expansion of the smoke-containing inert gas as it leaves the condensation cell, allowing the generation of intense beams of large positive and negative cluster ions. We refer to the unique union of these two techniques as the Smoke-Ion Source. Below, we describe the Smoke-

Ion Source along with its associated apparatus, and present the results of mass spectrometric investigations involving cluster ions of lead, lithium, sodium, and magnesium; mixed cluster ions of lithium and magnesium; and cluster ions of lithium oxide and magnesium oxide.

EXPERIMENTAL

A schematic diagram of the Smoke-Ion Source is presented in Figure 1. The material of interest is evaporated from a heat shielded crucible (capable of achieving temperatures to 2,300 K) by direct resistive heating. The assembly containing the crucible is separated from the inert gas condensation cell by a water-cooled copper box which thermally isolates the cool inert gas from the high temperature environment of the crucible region. Vapor effusing from the crucible enters the condensation cell, which typically contains from 0.5 to 10 torr of helium and can be maintained at constant temperatures between 77 K and 285 K by a coolant reservoir. The cool inert gas thermally quenches the vapor, causing supersaturation with subsequent nucleation and cluster growth. Metal oxide cluster formation is accomplished by doping the inert gas with a small percentage (0.5-2.5 %) of reactant gas (typically O_2). The condensation cell is coupled to high vacuum by a small (1.0-2.5 mm diameter) aperture, creating a flow of helium which entrains the clusters and transports them into the high vacuum region via a weak jet expansion. A negatively biased hot filament injects low energy electrons into the smoke-containing helium flow immediately as it exits the aperture. The presence of axial magnetic fields in the expansion region greatly enhances cluster ion production. The entire source is electrically floated at either ± 500 V or

± 1 kV with respect to ground potential. This electron injection configuration is used to generate both positive and negative cluster ions.

The resulting beam of cluster ions and accompanying neutrals is skimmed before entering the remaining part of the apparatus. Briefly, this consists of an ion optical beam line, an ExB mass separator (Wien filter) and a Faraday cup for ion detection. The Wien filter can be operated at a high electrostatic field where it achieves normal mass resolution over a limited mass range, or at a low electrostatic field where it exhibits poor resolution but over a much larger mass range. The latter mode is particularly useful for detecting very large cluster ions.

GENERATION OF METAL AND METAL OXIDE CLUSTER IONS

(1) Lead: Cluster ions of lead were generated under two different sets of source conditions.¹ The first set employed a source aperture diameter of 1.0 mm, a helium pressure of 6.0 torr maintained at 195 K, and a crucible temperature of 1,460 K. Figure 2 presents mass spectra for both positive and negative lead cluster ions recorded under these conditions. In order to obtain these spectra, the Wien filter was operated in its high mass range mode. Both spectra exhibit a progression of unresolved cluster ion peaks ranging from approximately 40-400 atoms per cluster ion, and for both ion polarities, the intensity maximum in the size distribution corresponds to ~200 atoms per cluster ion. Assuming these cluster ions are spherical in shape, their diameters can be estimated through the expression $D = 2 Z^{1/3} R_S$, where D is the cluster diameter, Z is the total number of valence electrons in the cluster, and R_S is the Wigner-Seitz radius of the bulk metal. These lead cluster ions are estimated to range in size from ~15-30 Å in diameter with the

peak of the size distribution at ~ 20 Å. In the anion spectrum, an ion current of 600 pA was observed at this maximum. If average currents of cluster anions are compared, this is about five orders of magnitude more intense than those available via laser vaporization techniques.¹³ In the cation mass spectrum, a series of low mass peaks due to Pb^{++} and $\text{Pb}_{n=1-3}^+$ was observed in addition to the high mass distribution. Interestingly, these low mass peaks were absent in the anion spectrum, suggesting the small lead cluster cations may have resulted from fragmentation. However, the similarity between the high mass distributions in the cation and anion spectra may indicate that they reflect the neutral cluster distribution.

In an effort to explore the source's ability to access different cluster ion size distributions, a second set of source conditions was selected. This set utilized a source aperture diameter of 1.5 mm, a helium pressure of 1.6 torr at 273 K, and a crucible temperature of 1,460 K. Figure 3 shows the resultant lead cluster anion mass spectrum with the Wien filter operating in its low mass range mode. A variety of small lead cluster anions was observed demonstrating the ability to shift the cluster ion size distribution by manipulating source conditions.

(2) Lithium: Negatively and positively charged clusters of lithium were generated utilizing a 2.0 mm diameter source aperture, 1.5 torr of He at 273 K, and a crucible temperature of 1,100 K. Figure 4 presents a typical mass spectrum of lithium cluster anions generated under these conditions. This set of source conditions produced lithium cluster ion distributions that ranged from 650-2,800 atoms per cluster ion ($D \cong 30-50$ Å). The intensity maximum in the size distribution corresponded to about 1,200 atoms per cluster ion ($D \cong 35$ Å). By utilizing slightly higher He pressures in the condensation

cell (3-5 torr), cluster anions comprised of 11,500 lithium atoms ($D \cong 80 \text{ \AA}$) have been generated.

(3) Sodium: Cluster anions of sodium were generated utilizing a 2.0 mm diameter source aperture, 1.9 torr of He at 273 K, and a crucible temperature of 785 K. Figure 5 presents the mass spectrum of sodium cluster anions generated using these conditions. A sodium cluster anion distribution that ranged from 700 ($D \cong 35 \text{ \AA}$) to well beyond 1,750 ($D \cong 50 \text{ \AA}$) atoms per cluster anion was observed. The intensity maximum in the size distribution corresponded to about 1,250 atoms per cluster anion ($D \cong 45 \text{ \AA}$).

(4) Magnesium: Cluster anions of magnesium were generated utilizing a 2.0 mm diameter source aperture, 1.2 torr of He at 273 K, and a crucible temperature of 975 K. The resultant magnesium cluster anion distribution ranged from 150-850 ($D \cong 20\text{-}35 \text{ \AA}$) atoms per cluster anion, with the intensity maximum in the size distribution at 375 atoms per cluster anion ($D \cong 25 \text{ \AA}$).

(5) Lithium-Magnesium: Mixed lithium-magnesium cluster anions were generated by evaporating lithium and magnesium metals from separate chambers in a single crucible at a temperature of 1,015 K. The evaporation rates per unit area of each metal were controlled so that the ratio of Mg to Li atoms in precondensed metal vapor would be 3:1. Other source conditions used included 1.2 torr of He maintained at 273 K and a 2.0 mm diameter source aperture. The mass spectrum of mixed lithium-magnesium cluster anions recorded under these conditions is presented in Figure 6. The $(\text{Li}_x\text{Mg}_y)^-$ cluster anions observed ranged in mass from ~2,000 amu to well over ~20,000 amu with the intensity maximum of the mass distribution at ~7,000 amu. The ion current at this maximum measured approximately 1 nA.

(6) Metal Oxides: Oxides of lithium and magnesium cluster anions were generated under essentially the same source conditions used to generate pure metal cluster anions, but a small percentage of O_2 was added to the helium inert gas. In the case of the lithium-oxygen system, 1.5 % O_2 in helium was used in the condensation cell. The resultant mass spectrum, presented in Figure 7, shows a series of unresolved $(Li_xO_y)^-$ cluster anions as well as O^- and O_2^- . For the formation of $(Mg_xO_y)^-$ anions, 1.0 % oxygen in helium was used in the condensation cell. The resultant mass spectrum, presented in Figure 8, was recorded with the Wien filter operating in its low mass range mode. Peaks corresponding to $(Mg_xO_y)^-$ cluster anions of various stoichiometries are evident along with O_2^- and O^- . In both cases, the addition of small amounts of oxygen to the condensation cell dramatically lowered the sizes of the particles produced in the source.

CONCLUSION

We have shown the Smoke-Ion Source to be a powerful and versatile tool for generating intense beams of positive and negative cluster ions comprised of metals and metal oxides. Future experiments with the Smoke-Ion Source fall into one of two categories. The first category will involve the generation of cluster ions from additional materials, and these experiments shall primarily be mass spectrometric in nature. The second category involves probing the electronic energy levels of the clusters and cluster ions produced by this source. Negative ion photoelectron spectroscopy performed on size-selected cluster anions will reveal the ground and low-lying excited electronic state structure of a cluster anion's corresponding neutral (at the anion geometry). In addition, photodestruction and photodissociation experiments will be

performed on size-selected beams of positive and negative cluster ions to examine Mie-like resonances and other photoabsorption processes in these systems.

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REFERENCES

1. K. M. McHugh, H. W. Sarkas, J. G. Eaton, C. R. Westgate, and K. H. Bowen, *Z. Phys. D* **12**, 3 (1989)
2. A. Yokozeki and G. D. Stein, *J. Appl. Phys.* **49**, 2224 (1978)
3. D. M. Mann and H. P. Broida, *J. Appl. Phys.* **44**, 4950 (1973)
4. T. P. Martin, *J. Chem. Phys.*, **81**, 4426 (1984)
5. J. Mühlbach, P. Pfau, K. Sattler, and E. Recknagel, *Z. Phys. B.* **47**, 233 (1982)
6. F. Frank, W. Schulze, B. Tesche, J. Urban, and B. Winter, *Surf. Sci.* **156**, 90 (1985)
7. S. J. Riley, E. K. Parks, C. R. Mao, L. G. Pobo, and S. Wexler, *J. Phys. Chem.* **86**, 3911 (1982)
8. A. E. T. Kuiper, G. E. Thomas, and W. J. Schouten, *J. Cryst. Grow.* **51**, 17 (1981)
9. R. W. Farley, P. J. Ziemann, R. G. Keesee, H. Funasaka, and A. W. Castleman, Jr., to be published
10. H. Haberland, H. G. Schindler, and D. R. Worsnop, *Ber. Bunsenges. Phys. Chem.* **88**, 270 (1984)
11. J. V. Coe, J. T. Snodgrass, C. B. Freidhoff, K. M. McHugh, and K. H. Bowen, *J. Chem. Phys.* **84**, 618 (1986)
12. M. L. Alexander, M. A. Johnson, N. E. Levinger, and W. C. Lineberger, *Phys. Rev. Lett.* **57**, 976 (1986)
13. O. Cheshnovsky, C. L. Pettiette, and R. E. Smalley, in *Ion and Cluster Ion Spectroscopy and Structure*, ed. J.P. Maier (Elsevier, Amsterdam, 1989), p. 373

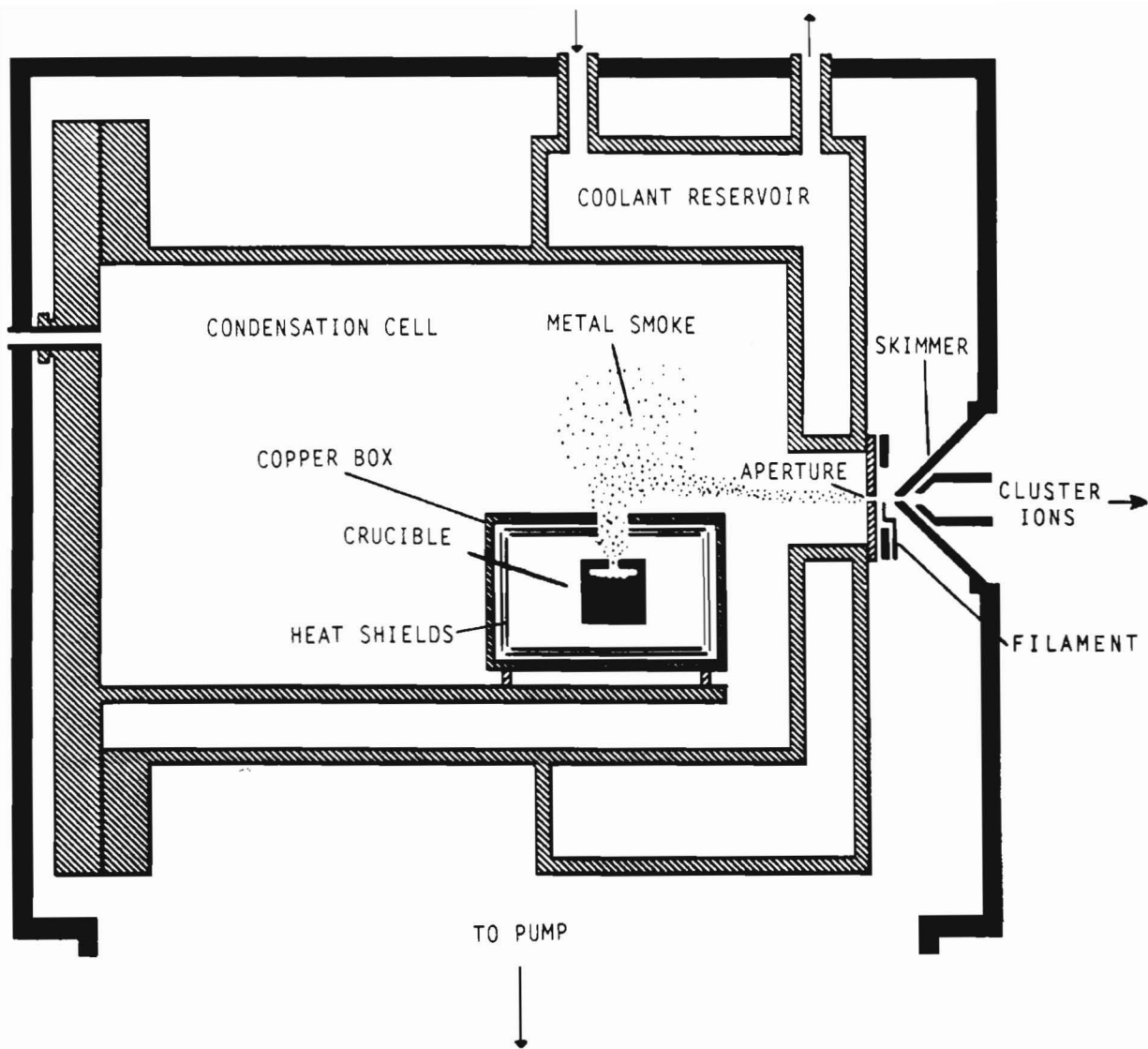


FIGURE 1. SCHEMATIC DIAGRAM OF THE SMOKE-ION SOURCE

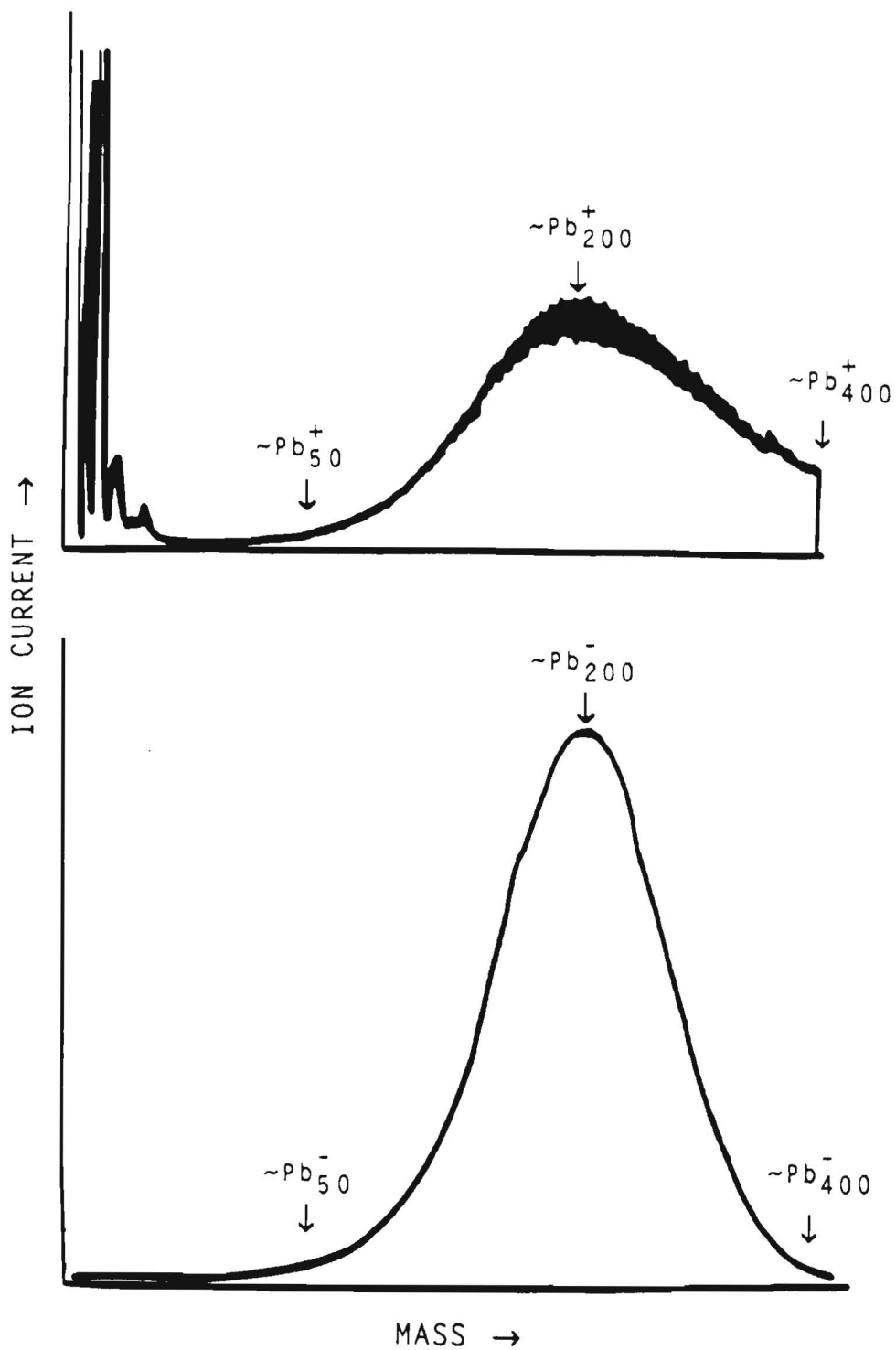


FIGURE 2. MASS SPECTRA OF LARGE POSITIVE AND NEGATIVE CLUSTER IONS OF LEAD GENERATED BY THE SMOKE-ION SOURCE

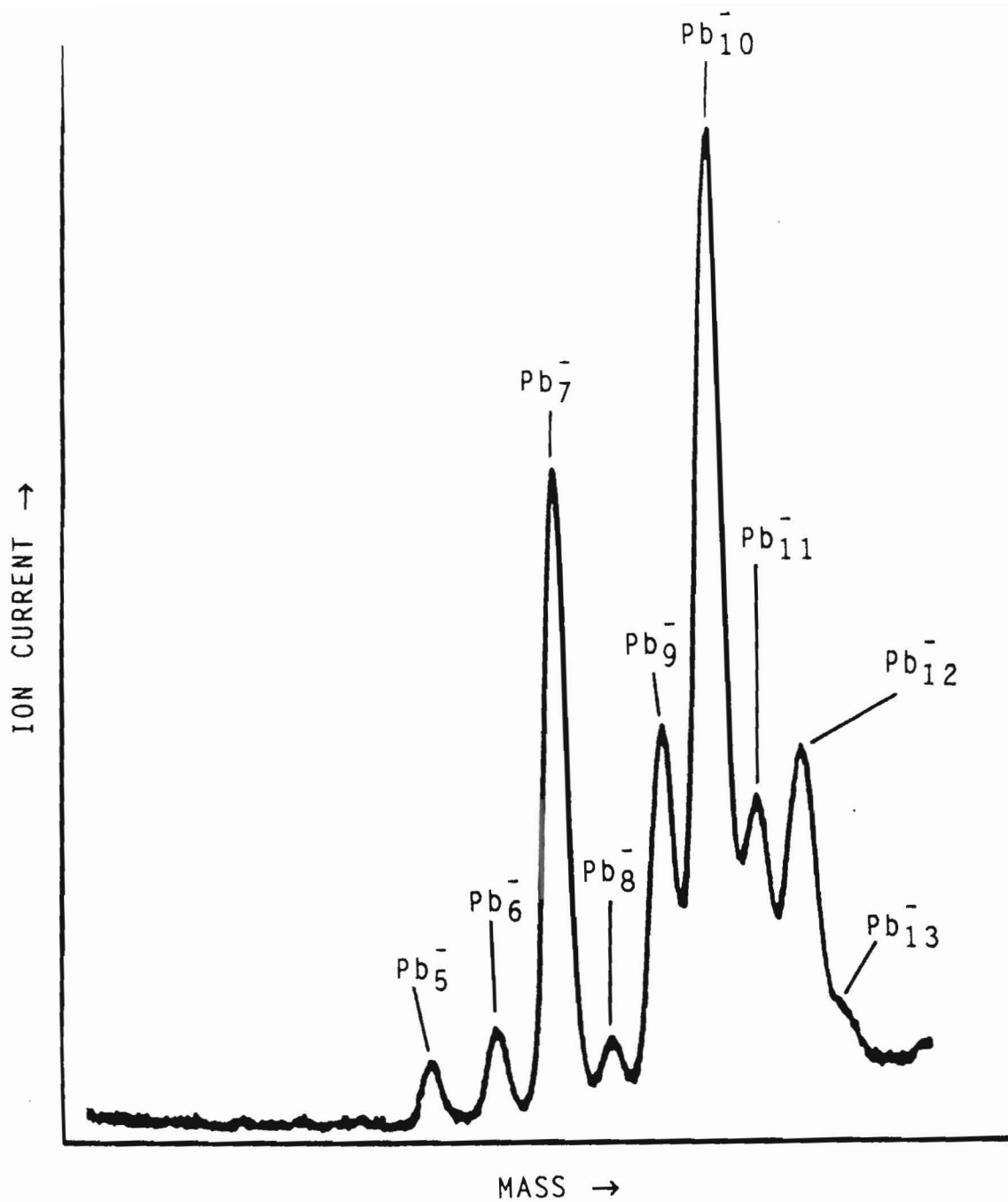


FIGURE 3. MASS SPECTRUM OF SMALL LEAD CLUSTER ANIONS GENERATED USING THE SMOKE-ION SOURCE

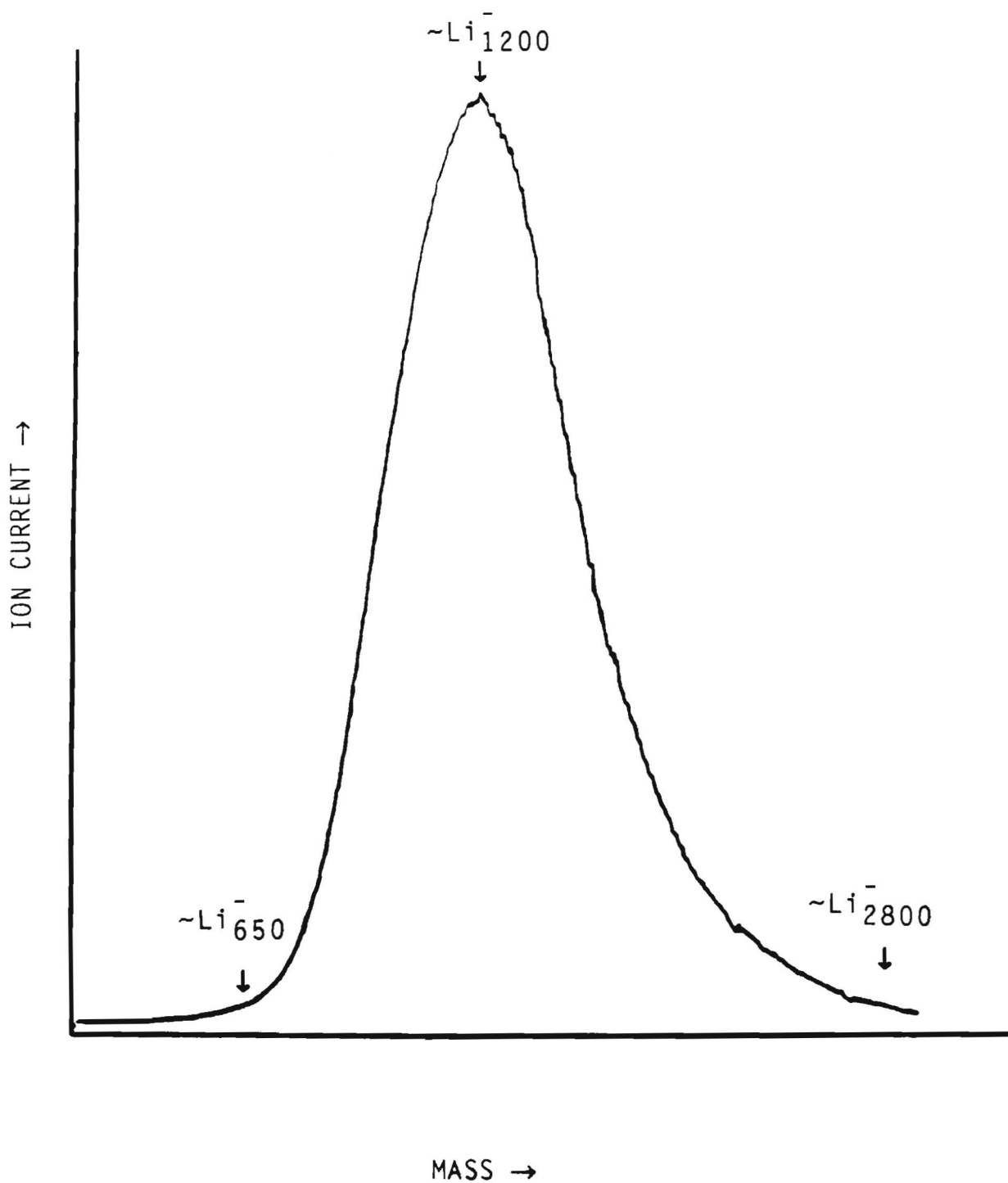


FIGURE 4. MASS SPECTRUM OF LARGE NEGATIVE CLUSTER IONS OF LITHIUM GENERATED BY THE SMOKE-ION SOURCE

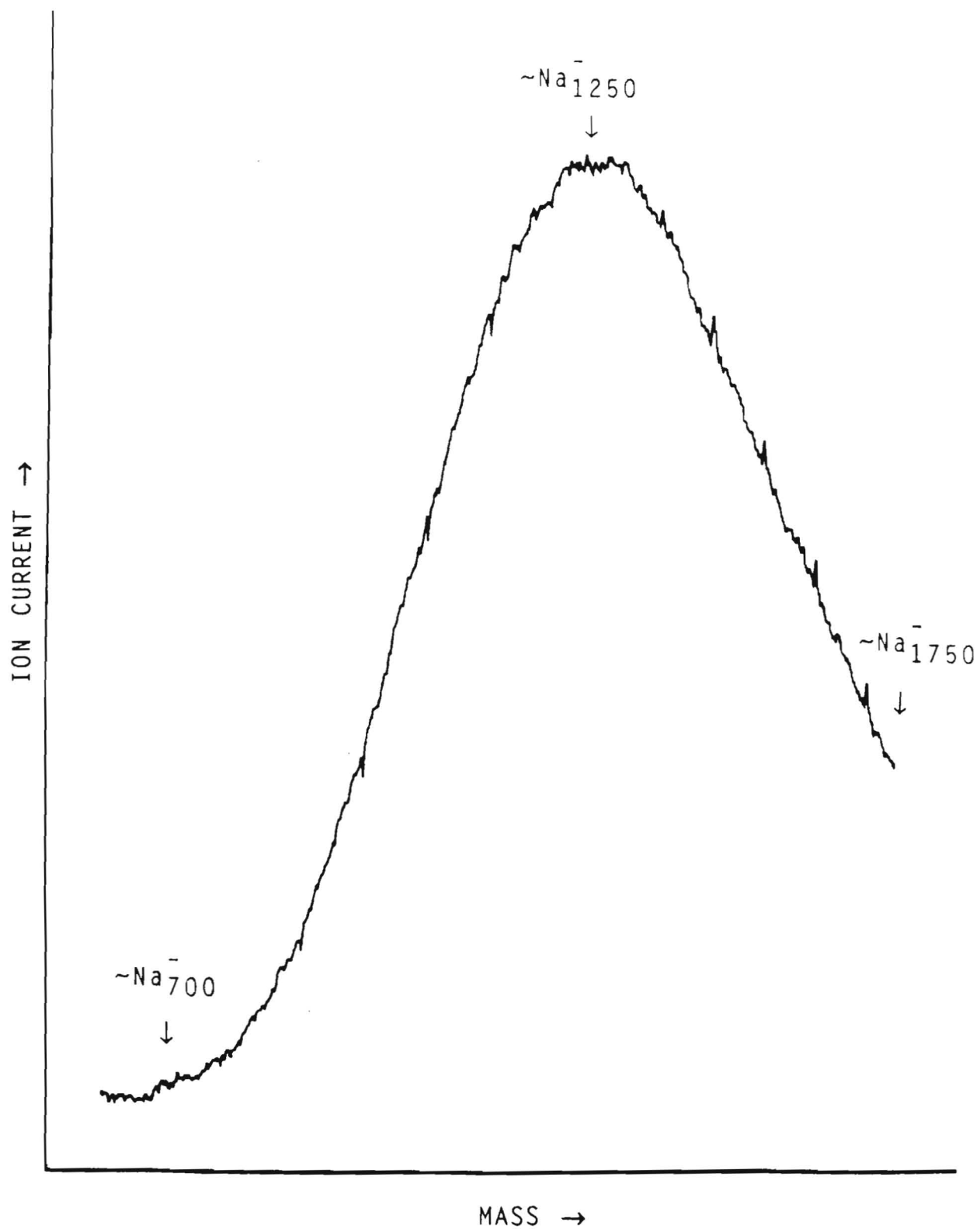


FIGURE 5. MASS SPECTRUM OF LARGE NEGATIVE CLUSTER IONS OF SODIUM GENERATED BY THE SMOKE-ION SOURCE

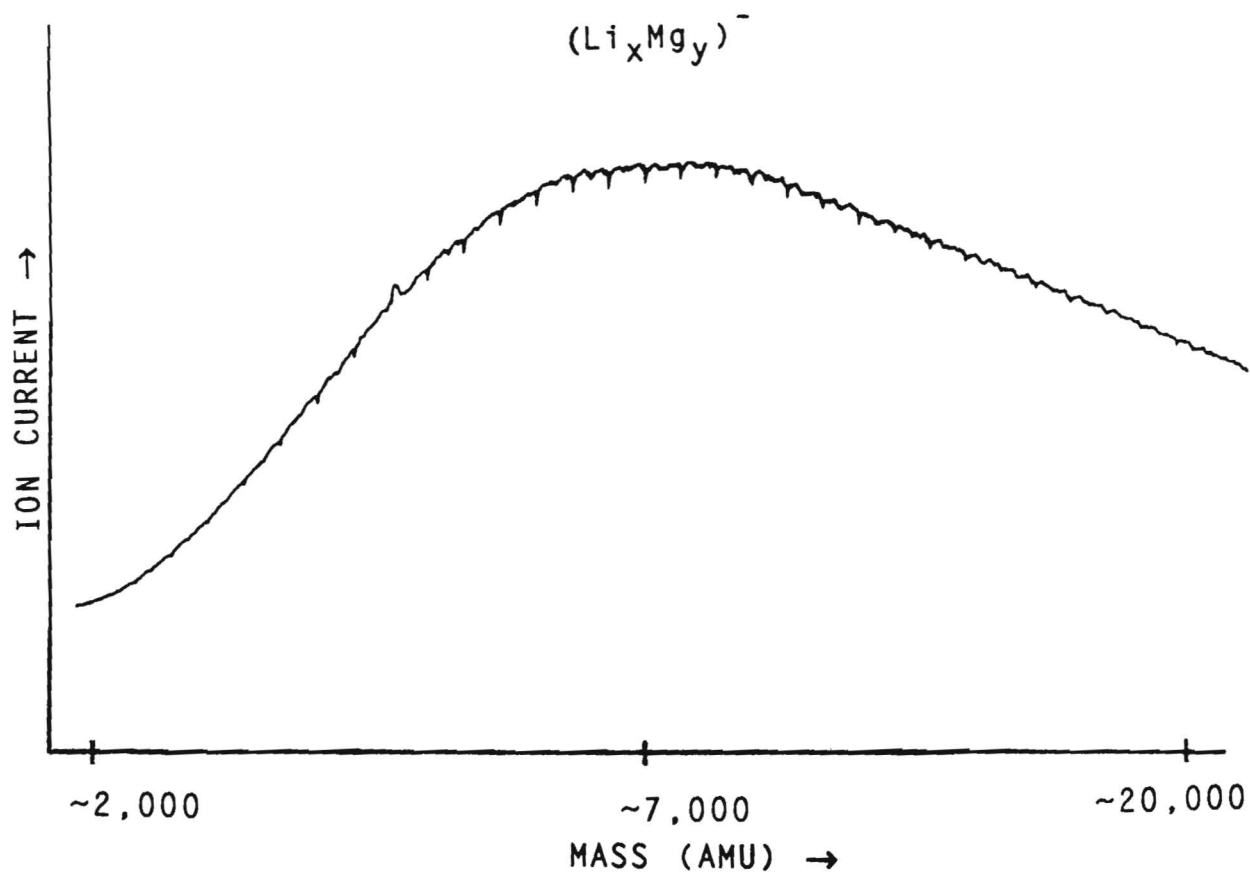


FIGURE 6. MASS SPECTRUM OF LARGE LITHIUM-MAGNESIUM CLUSTER ANIONS GENERATED BY THE SMOKE-ION SOURCE

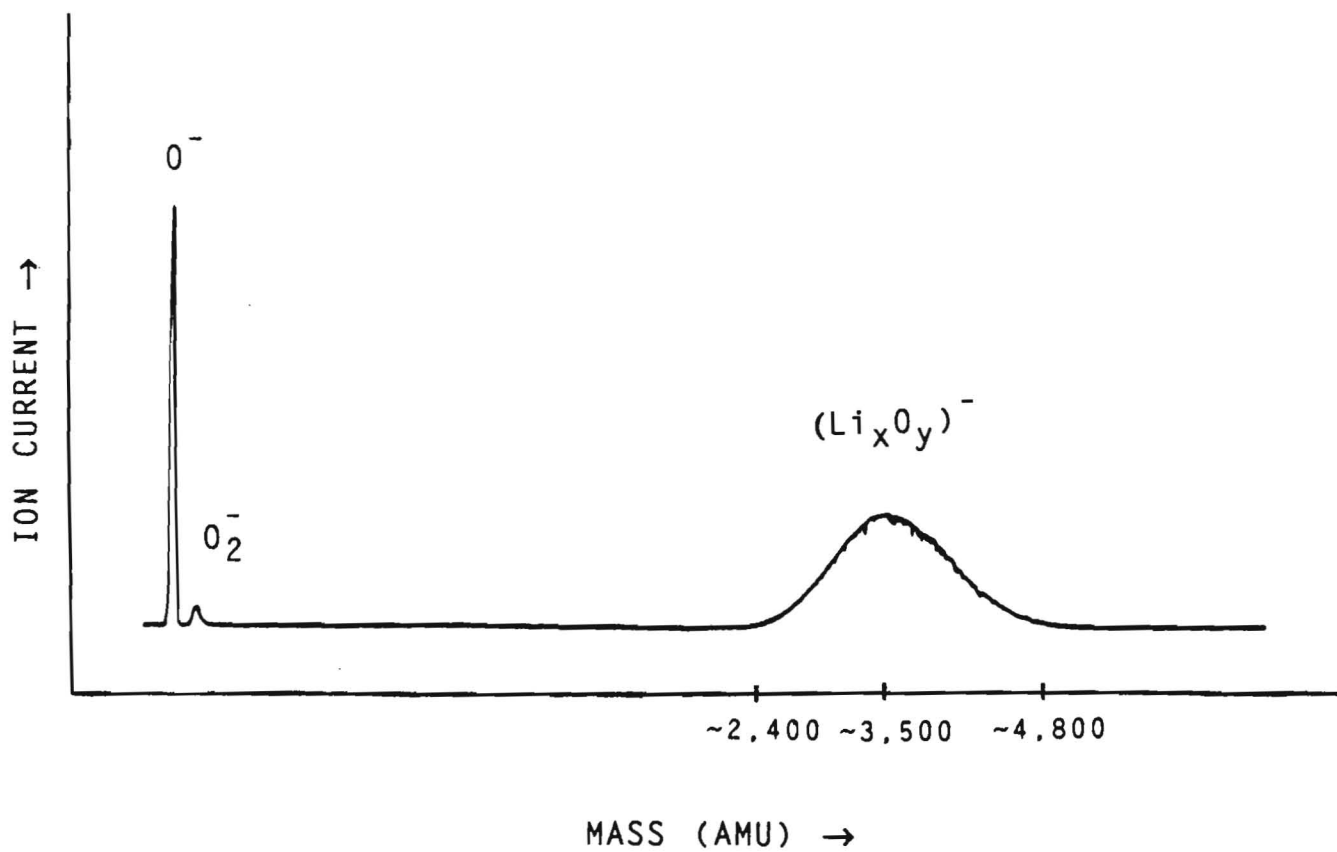


FIGURE 7. MASS SPECTRUM OF LARGE $(\text{Li}_x\text{O}_y)^-$ CLUSTER ANIONS, ALONG WITH O_2^- AND O^- , GENERATED USING THE SMOKE-ION SOURCE

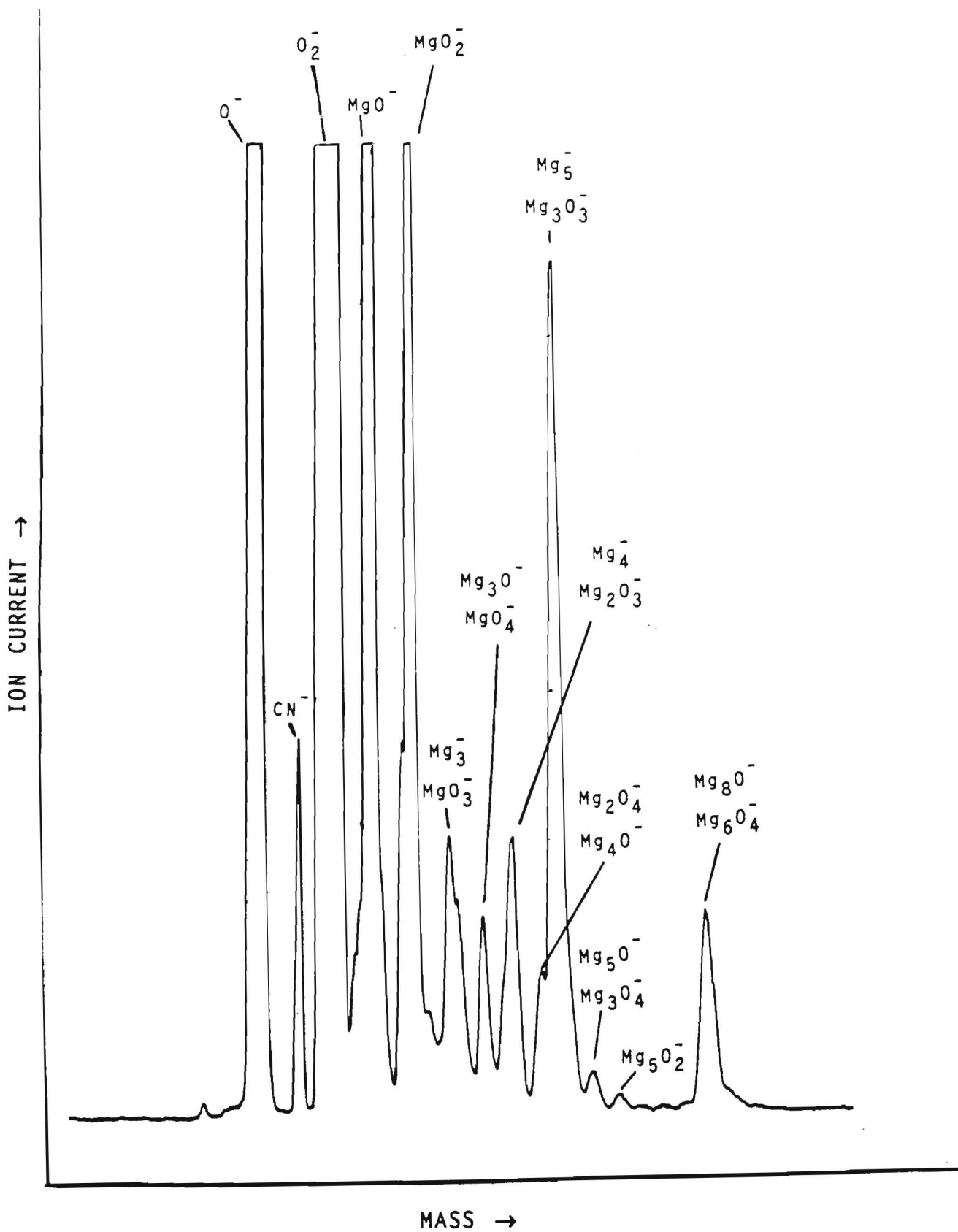


FIGURE 8. MASS SPECTRUM OF SMALL $(Mg_xO_y)^-$ CLUSTER ANIONS, ALONG WITH O_2^- AND O^- , GENERATED USING THE SMOKE-ION SOURCE