



## I. GENERAL REPORT

## A. Introduction

This is the ninth progress report for this project covering the six-month period January 1, 1975 to July 1, 1975. Funds from the E.R.D.A. were used to support a continuing program at the Cyclotron Institute of Texas A&M University.

## B. Summary of Activities

A new experiment involving the comparison of beta-gamma directional correlations for mirror decays  $^{20}\text{F}(\beta^-)^{20}\text{Ne}^*$  (1.63 MeV) and  $^{20}\text{Na}(\beta^+)^{20}\text{Ne}$  (1.63 MeV) has been instigated to search for second-class currents in nuclear beta decay. Developmental work on the production of  $^{20}\text{F}$  and  $^{20}\text{Na}$  using the He-jet technique has been completed and strong sources are now available.

The study of beta-neutrino correlations as a function of decay energy in the mass-8 system was continued and preliminary results obtained for  $^8\text{Li}$ . The correlation coefficients measured show a small energy-dependent variation from -0.33 indicating possible meson exchange or second-class current contributions.

Development of the  $^{252}\text{Cf}$ -plasma desorption mass spectrometer has continued and its application to atomic mass work examined. Excellent precision and accuracy have been found and masses can be measured to 0.5 milli amu.

Studies continued on the desorption of chemical targets using energetic heavy ions from  $^{252}\text{Cf}$  decay. Mass spectra have been measured for a wide variety of involatile compounds including several thermally-labile biological molecules which could not be studied using conventional

mass spectroscopy. A particularly significant result was the desorption of the 15-residue peptide gramicidin-A which may have opened a new frontier in mass spectroscopy research. The studies have confirmed that  $^{252}\text{Cf}$ -plasma desorption is an important new application of nuclear energy.

#### C. Personnel

1. Principal Investigator, R. D. Macfarlane, Professor of Chemistry
2. Senior Scientist, D. F. Torgerson
3. Research Associate, K. Chung
4. Graduate Students
  - a. C. Alton Hassell, B.S. Baylor University 1969
  - b. R. P. Skowronski, B.S. Michigan 1970
  - c. Larry Speigel, B.S. Reed College 1973
  - d. Duane Piper, B.S. LeTourneau College 1973
  - e. Rodney Kadrmus, B.A. (chemistry) Dickinson State College 1975
5. Undergraduate Assistants
  - a. Mark Clemenson
  - b. Harry Tang
  - c. Catherine McNeal
  - d. Creston Gay

#### D. Facilities Used

Approximately 24 hours of cyclotron beam are used each month. The Cyclotron Institute's IBM 7094 was used for all data analysis and the PDP 15/40 computer was used for on-line data acquisition. The mass spectrometers were constructed using cyclotron facilities and some of the repair/maintenance work is performed by the Cyclotron Institute

staff. A new low-humidity counting room has been constructed adjacent to the mass spectrometers to house our electronics. In general, the support of the Cyclotron Institute's staff has been crucial to the development of our program.

#### E. Publications and Presentations

1. Work published or accepted for publication for the period January 1 to July 1, 1975:

"Atomic Mass Measurements Using Time-of-Flight Mass Spectroscopy," D. F. Torgerson, R. D. Macfarlane, and L. S. Spiegel, Proceedings of the Fifth International Conference on Atomic Masses, Paris, 1975 (in press).

#### 2. Invited Lectures

R. D. Macfarlane

"<sup>252</sup>Cf-Plasma Desorption Mass Spectroscopy," Chemistry Dept., Stanford Univ., February 1975; Chemistry Dept. Univ. of California at Berkeley, February 1975; Chemistry Dept., Oklahoma State Univ., January 1975; Rockefeller Univ., June 1975; Sloan-Kettering Institute for Cancer Research, June 1975.

Invited Consultant, NIH Workshop on Mass Spectroscopy, May 1975

D. F. Torgerson

"<sup>252</sup>Cf-Plasma Desorption Mass Spectroscopy: A New Application of Nuclear Particles," Physics Dept., Univ. of Erlangen-Nürnberg, June 1975; Physics Dept., Univ. of Munich, June 1975; Physics Dept., Technical University, Darmstadt, June 1975.

"A New Approach to  $\beta$ - $\nu$  Correlation Measurements in Nuclear Beta Decay," Physics Dept., Univ. of Erlangen-Nürnberg, June 1975.

"Mass Spectroscopy of Involatile Compounds," National Institutes of Health Workshop on Mass Spectroscopy, May 1975.

Invited consultant, NIH Workshop on Mass Spectroscopy, May 1975.

3. Talks Presented at Meetings

"A New Approach to Time-of-Flight Mass Spectroscopy," D. F. Torgerson and R. D. Macfarlane, 23rd Annual Conf. on Mass Spectroscopy, Houston, 1975.

"Surface Chemical Ionization of Arginine and Two Isobaric Peptides," R. D. Macfarlane, R. Skowronski, C. A. Hassell, and D. F. Torgerson, 23rd Annual Conference on Mass Spectroscopy, Houston, 1975.

## II. ABSTRACTS OF WORK PUBLISHED OR ACCEPTED FOR PUBLICATION

- A. Atomic Mass Measurements Using Time-of-Flight Mass Spectroscopy,  
D. F. Torgerson, R. D. Macfarlane, and L. S. Spiegel, Proceedings  
of the Fifth International Conference on Atomic Masses, Paris, 1975  
(in press)

We describe herein a new approach to precise mass measurements using time-of-flight mass spectroscopy. The spectrometer has been designed to operate in the "on-line" mode coupled with the He-jet system,<sup>1</sup> or to be used off-line with stable species.<sup>2</sup> Although time-of-flight mass spectroscopy is not normally associated with precision work, accurate mass measurements can in principle be accomplished by the use of long flight paths and modern timing instrumentation. It is the long-range goal of this work to directly measure the masses of nuclei far from stability.

## III. COMPLETED WORK

A.  $^{252}\text{Cf}$ -Plasma Desorption Mass Spectroscopy of Involatile Molecules

$^{252}\text{Cf}$ -plasma desorption mass spectroscopy (PDMS) was originally envisioned for off-line developmental work using the MAGGIE beta-recoil mass spectrometer. In the past 6 months, however, the system has been used to probe several involatile biomolecules sent to us from outside laboratories. These samples were, in general, sent to us only after all other attempts using conventional mass spectroscopy had failed. Some of the more interesting examples of this work are now summarized. By studying a broad class of compounds, the mechanism for PDMS is becoming understood.

## 1. Xanthine-Tyrosine

This molecule is being studied by Stöhrer as a model for understanding protein-nucleic acid interactions. Attempts to obtain the mass spectrum of the parent molecule had failed and the structure was thus not confirmed. The PDMS technique, however, led to  $(M + 1)^+$  and  $(M - 1)^-$  ions in good yield and the proposed structure was confirmed. In the positive ion spectrum, quasimolecular ions containing Na and K were also observed, the yield being dependent on the alkali metal ion intensity in the mass spectrum.

We now believe that ion production predominantly involves  $\text{H}^+$  ion transfer within a vaporized dimer, leading to  $(M + 1)^+$  and  $(M - 1)^-$  ions. Alkali metal attachment appears to occur on a neutral molecule or dimer prior to the formation of the ion pair as increasing the  $\text{Na}^+$

concentration in the sample does not alter the  $(M - 1)^-$  intensity but greatly increases the  $(M + Na)^+$  yield, reducing the  $(M + 1)^+$  intensity to often undetectable levels.

2. Sulfuric Acid Esters (p-nitrocatechol  $SO_4$ , estrone-3- $SO_4$ , estrioltrisulfate, glucose-6- $SO_4$ )

Sulfuric acid esters are an important class of natural product molecules having low volatility and whose analysis has been virtually ignored due to the experimental problems encountered. These compounds also have relevance to pollution-control studies. We have used the  $^{252}Cf$  PDMS technique to obtain mass spectra of the sodium and potassium salts of these compounds and in all cases detect quasimolecular ions. As an alkali metal, in this case, replaces the labile H, the vaporized dimer exchanges an alkali metal ion leading to ions of the form  $(M + K)^+$  and  $(M - K)^-$ . This is a significant result as the transfer of alkali metal ions may be a "softer" process because of the lower acid strength and lack of hydrogen bonding. Thus, extremely thermally-labile molecules may be more amenable to the  $^{252}Cf$  PDMS method if their salts are used.

## IV. WORK IN PROGRESS

## A. Beta-Gamma Directional Correlations and Second-Class Currents in Nuclear Beta Decay (with R. E. Tribble, Phys. Dept., Texas A&amp;M Univ.)

The existence or absence of second-class currents (SCC) in nuclear beta decay is still an open question as conflicting data have been reported. In order to unambiguously measure a possible SCC contribution to the beta decay process, all other contributions must be known or eliminated including the dominant first-class allowed terms and nuclear structure effects. It is generally acknowledged that correlation experiments involving mirror decays offer the best opportunity for observing the SCC.

Our approach is to use the mass-20 system as a laboratory to search for the existence of the SCC. We are presently measuring the  $\beta$ - $\gamma$  directional correlations for the  $\beta^-$  decay of  $^{20}\text{F}$  to the 1.63 MeV level in  $^{20}\text{Ne}$  and comparing the correlation to the analogous  $\beta^+$  decay of  $^{20}\text{Na}$  to the same level. These are Gamow-Teller decays which include first-class axial vector, second-forbidden and weak magnetism contributions, as well as a possible SCC. By subtracting the two correlations, however, all contributions which do not change sign under G-parity are eliminated leaving the weak magnetism and SCC terms. The weak magnetism contribution can be calculated from the M1 analog decay strength using CVC theory. Thus, the experiment isolates the desired quantities and should produce conclusive evidence for or against the existence of the SCC.

Activity is being produced via the  $^{19}\text{F}(d,p)^{20}\text{F}$  and  $^{20}\text{Ne}(p,n)^{20}\text{Na}$  reactions employing the He-jet recoil transport method to produce thin

sources. (Developmental work involving the chemistry of the He-jet technique has led to abundant yields of these nuclei.) The correlation chamber has been built and preliminary data have recently been obtained to test geometries. Extensive tests are being performed to ensure that the source geometry is well-defined and a skimmer/nozzle system is being constructed to remove He from the radioactive beam.

#### B. Beta-Neutrino Directional Correlations in Mass-8

An alternative approach to measuring second-class currents in nuclear beta decay is to compare beta-neutrino correlations for mirror nuclei. We have developed over the past few years a new technique for extracting  $\beta$ - $\nu$  correlations from beta-delayed alpha and proton line shape data which has been described in previous reports.

Beta-neutrino correlations for  $^8\text{Li}$  decay to the broad alpha-decaying 2.94 MeV level in  $^8\text{Be}$  have been measured and some of the analysis has been completed. Activity produced from the  $^7\text{Li}(d,p)^8\text{Li}$  reaction was transported using the He-jet technique to a skimmer/nozzle system where the He was separated from the flow. The resulting beam was collimated and collected on a  $30 \mu\text{g}/\text{cm}^2$  VYNS foil. By measuring both alpha particles from the decay of the 2.94 MeV state in coincidence, alpha particle spectra as a function of level energy could be generated.

Some preliminary results of the line shape analysis for  $^8\text{Li}$  decay are shown in Fig. 1 where the  $\beta$ - $\nu$  correlation coefficient  $\alpha$  is plotted vs. the total beta decay energy  $W_0$ . According to the theory of Delorme and Rho, an energy-dependent departure from  $\alpha = -0.33$  is indicative of the presence of a SCC or exchange effects. The slope of the curve yields  $g^T/g_A \approx 2 \times 10^{-3}$  where  $g^T$  contains possible SCC and meson

exchange contributions. The definitive test, however, is the correlation measurement for the mirror decay  ${}^8\text{B}(\beta^+){}^8\text{Be}^*$  for which the slope of the  $q$  vs.  $W_0^+$  plot is predicted to change sign. Efforts are now being made to produce abundant amounts of  ${}^8\text{B}$  for these measurements.

### C. Atomic Mass Measurements

The MAGGIE time-of-flight mass spectrometer has been adapted for high resolution work for the measurement of precise masses. To test the precision, the  ${}^{252}\text{Cf}$ -plasma desorption technique was used to ionize and volatilize a thin  ${}^{148}\text{Sm}$  oxide film. Several intense mass peaks corresponding to combinations of  ${}^{148}\text{Sm}$  and O up to mass -1800 were observed.

A partial mass spectrum of the  ${}^{148}\text{Sm}$  oxide film is shown in Fig. 2. The exact mass of  ${}^{148}\text{SmO}$  was determined by using  ${}^{148}\text{Sm}$ ,  ${}^{148}\text{SmOH}$ , and  ${}^{148}\text{Sm}(\text{OH})_2$  groups as standards. Centroids were found by fitting Gaussian distributions to only the most intense 5 channels in the peak thereby avoiding any asymmetries due to tailing. The standards were then fit to a calibration curve. Nineteen spectra were analyzed in this manner and the  ${}^{148}\text{SmO}$  mass was determined to be  $163.90958 \pm 0.00049$ , 0.2 milli mass units away from the accepted literature value. This experiment demonstrated that both precision and accuracy could be obtained and that systematic errors were small.

Further developments to improve the resolution include the construction of a reflectron assembly to overcome the spread in the initial ion kinetic energies. Once the developmental work has been completed, the spectrometer will be placed on-line with the cyclotron for high-resolution radioisotope mass measurements.

D. <sup>252</sup>Cf-Plasma Desorption Mass Spectroscopy of Large Biomolecules

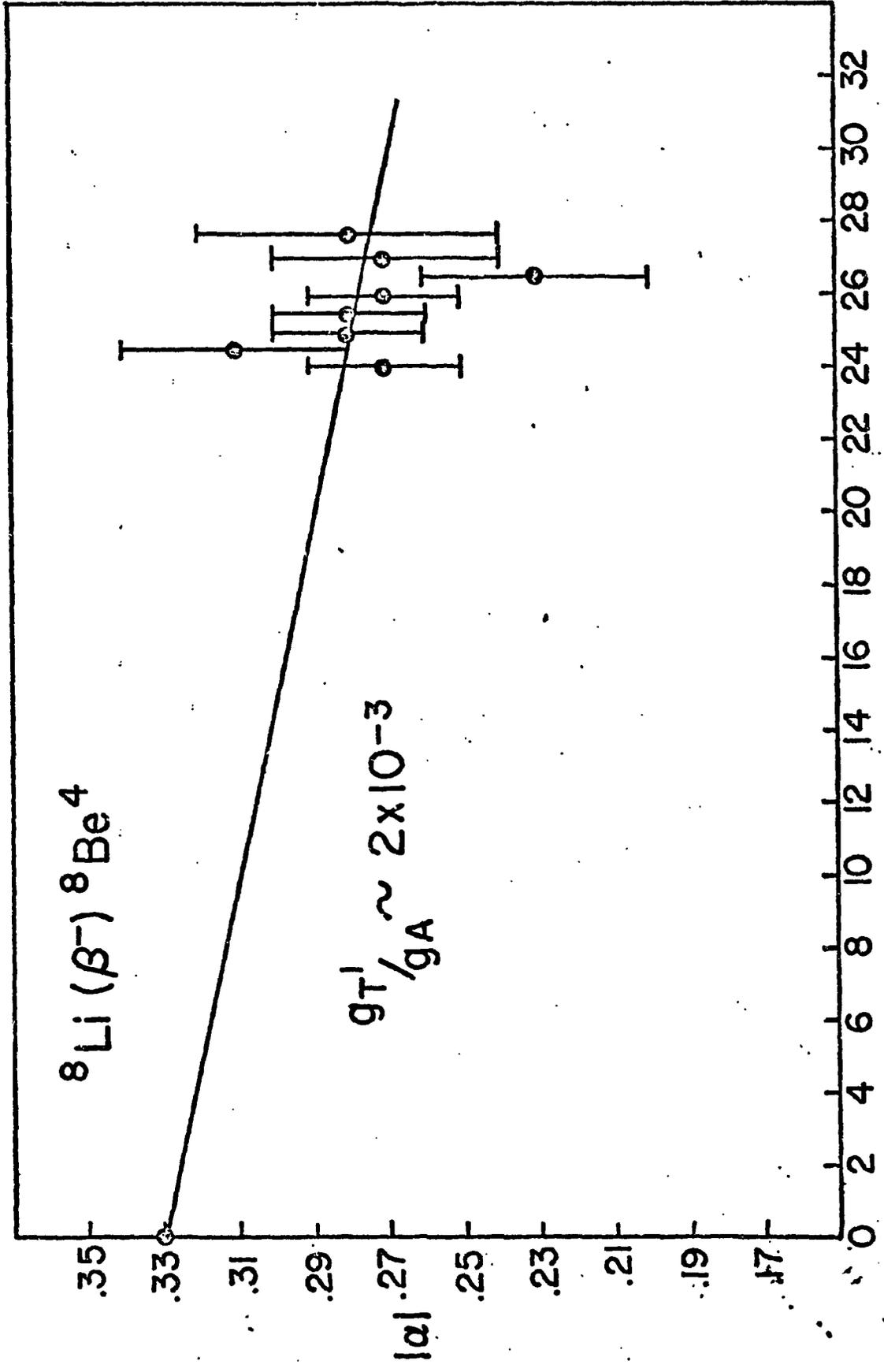
The volatility of large molecules whose polar groups have not been derivatized is generally extremely low due to strong intermolecular interactions in the solid state. As part of an exploratory program to investigate the application of <sup>252</sup>Cf PDMS to large biomolecules, a number of representative compounds have been studied.

Gramicidin-A is a well-known 15-residue natural peptide whose sequence and structure have been characterized. It exists in two forms differing by only the N-terminal amino acid residue which is L-valine or L-isoleucine. We have studied these molecules directly using PDMS and the positive ion mass spectrum for the mass range 1800-2000 is shown in Fig. 3. Quasimolecular ions (M + Na)<sup>+</sup> ions are characteristic of peptide spectra obtained using <sup>252</sup>Cf-PDMS when Na concentrations in the sample are high.

Positive results have also been obtained for cyanocobalamin (vitamin B12), a complicated molecule having a molecular weight of 1355.

The dinucleotide guanylyl (3'-5') adenosine (GpA) has also been studied and yields quasimolecular ions in high yield plus a fragmentation pattern in which characteristic ions can be identified. Efforts are continuing to develop procedures for studying even heavier biopolymers without derivatization. This is an important field of endeavor as no techniques are currently available for studying these classes of molecules despite their important physiological functions.

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WO  
Fig 1.  $\beta$ - $\nu$  Correlation Coefficients for  ${}^8\text{Li}$  as a function of decay energy

glassy  
55108

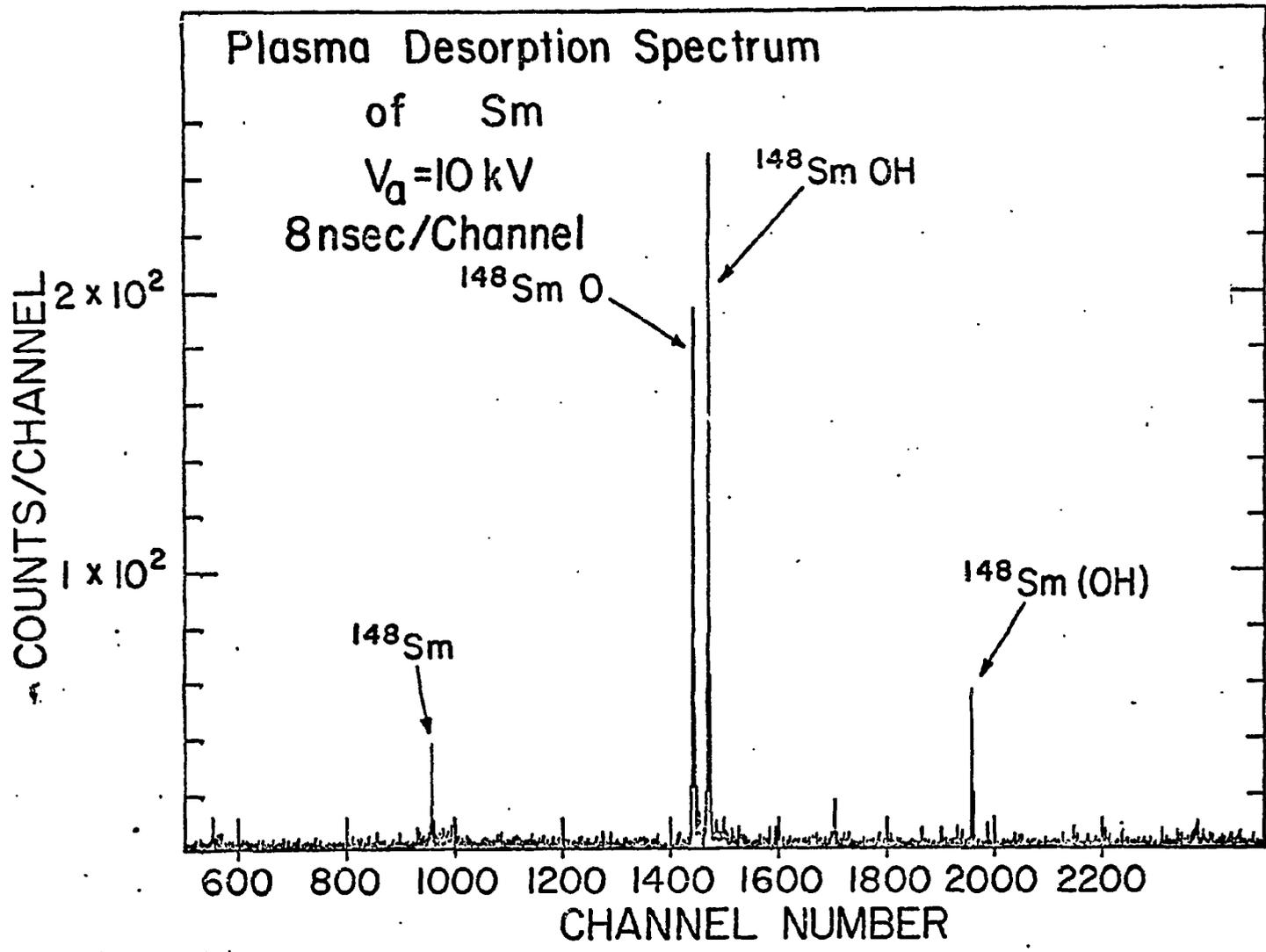


Fig. 2. PDMS of Samarium Oxide

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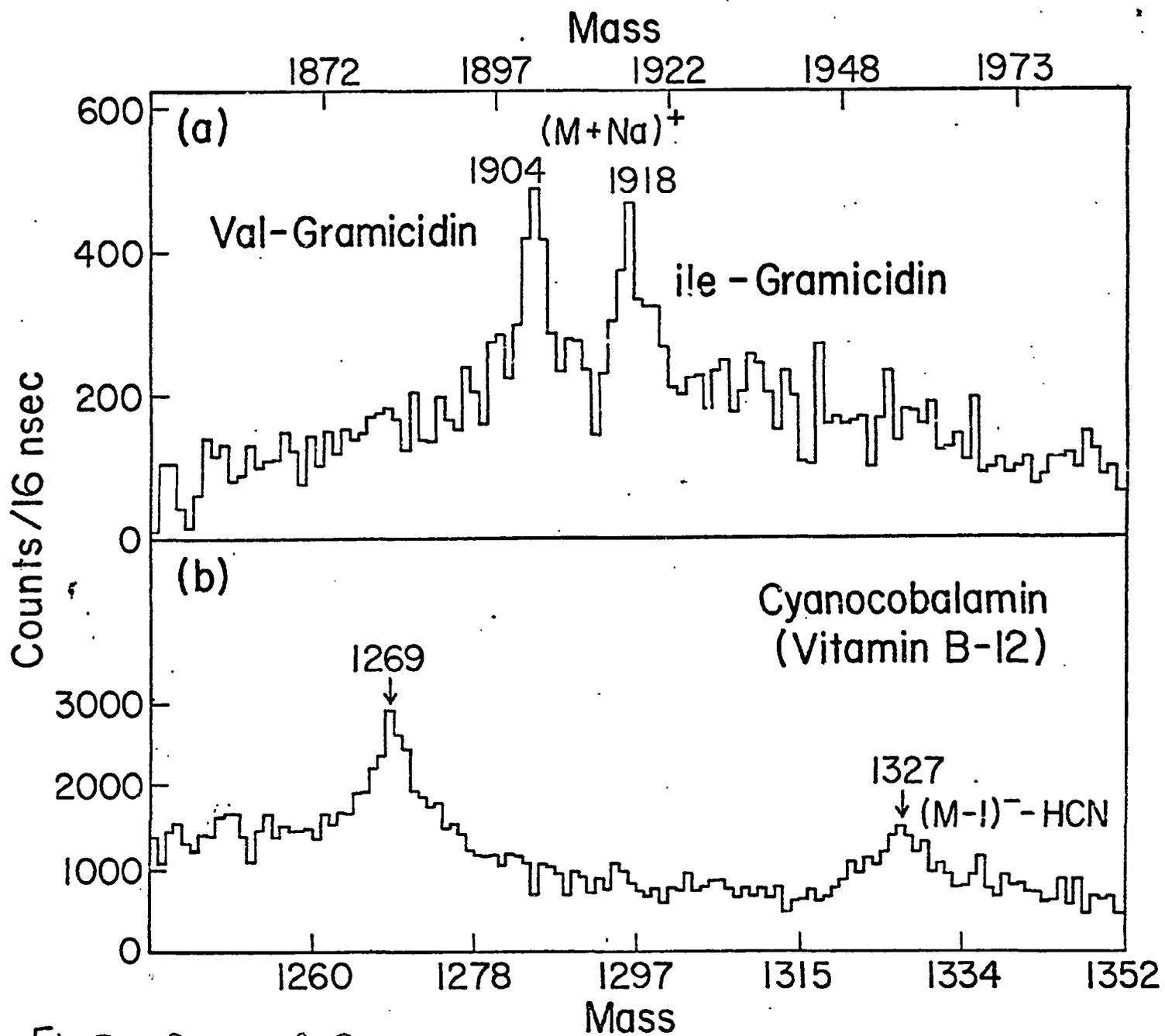


Fig 3. PDMS of Gramicidin and Cyanocobalamin