# Reanalysis of the *Pioneer Venus* Large Probe Neutral Mass Spectrometer data

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## Goals and motivation

The recent tentative detection of $PH_3$ by Greaves et al. (2020) has reignited a search for trace gases in the Venusian atmosphere. The mass spectrometer measurements from the Pioneer Venus probe—which sampled the lower 65 km of the atmosphere in 1978—are one of the few *in situ* datasets which can be used to evaluate the presence of $PH_3$. We set out to determine (1) whether $PH_3$ is present in the data, and (2) if there is any other new information in the LNMS data that can be extracted with modern data analysis techniques.

## Mass spectral deconvolution

We've updated the Monte Carlo algorithm of Gautier et al. (2020) to support moderate-resolution mass spectra, non-terrestrial isotope ratios, and low (<70 eV) ionization energies. We created a fragmentation pattern database with 37 molecules to represent a diverse range of possible atmospheric compositions. Our model allows the fragmentation patterns of our desired molecules to vary by 20%, and isotope ratios by 50% (except for D/H, which is unconstrained).

## LNMS instrument information

| | |
|---|---|
| **Mass analyzer type:** | magnetic sector |
| **Ionization type:** | electron impact (EI) |
| **Ionization energy:** | 22-70 eV |
| **Nominal resolution:** | M/ΔM = 440 (10% peak height) |
| **Mass range:** | 1-208 u |
| **Scan speed:** | 3.25 u/second |

## Mixing ratios and model spectra

**All four models shown here include a base composition of** $CO_2$, $N_2$, NO, $H_2O$, $H_2$, $SO_2$, COS, HCl, HF, Br, I, $C_6H_6$, noble gases, and calibration gases.

**Model 1: base only. Model 2: base + $H_2S$. Model 3: base + $PH_3$. Model 4: base + $H_2S$, CO, $O_2$,** and uses constraints from the PV LGC.

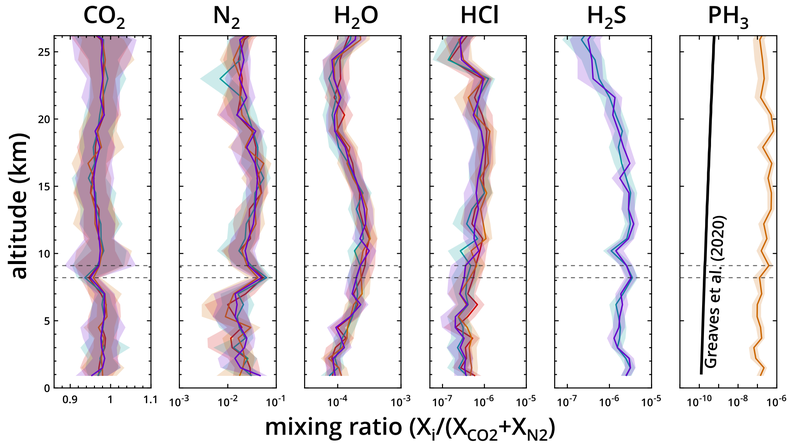



**Figure 1.** Retrieved mixing ratios below 26 km for four different composition models. Shaded region is 68% (1σ equivalent) interval. Dashed lines are low ionization energy scans. Mixing ratios generally agree with previous analyses of LNMS data (Hoffman et al. ,1980), but $PH_3$ mixing ratios are inconsistent with the results of Greaves et al. (2020).

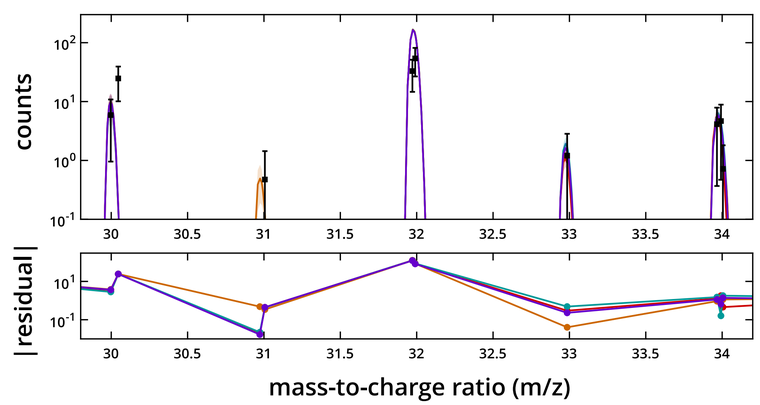
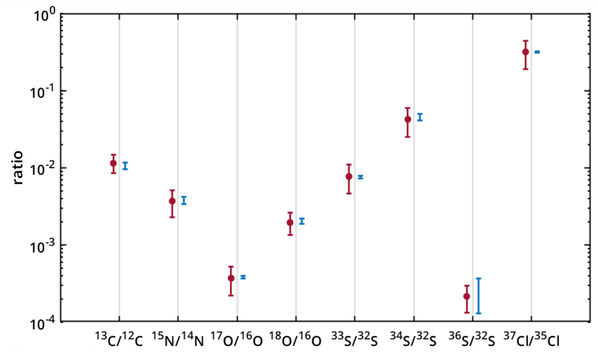



**Figure 2.** Model mass spectra at 51.3 km altitude using the same color scheme as above. Models with $H_2S$ and $PH_3$ both fit the data satisfactorily. However, the $PH_3$ abundance shown here would be several times greater than that predicted by Greaves et al. (2020).

## Isotope ratios for key elements




**LNMS, ratios from Model 1 (see left figure)**

**Range of natural terrestrial ratios**

**Figure 3:** Isotope ratios retrieved from LNMS for non-noble-gas elements integrated from 26km to the surface (black, error bars represent 68% interval). All ratios from LNMS are consistent with the terrestrial values. **(We also measure D/H, but that's too complicated for this poster!)**

## Future work and outstanding questions

Future work includes detailed sensitivity studies to show how changing model fit tolerances and prior distributions affect the output molecule abundances and isotope ratios. This model could also be used to analyze other Venus mass spectrometer data should other heritage data become available.

### Other outstanding questions include:

**What other species are consistent with the existing data? $NH_3$? Hydrocarbons?** A wide variety of molecules are consistent with the LNMS at ~ppm levels. In particular, C2 species are likely present (as internal contaminants), as indicated by peaks at 25-27 u.

**Will *DAVINCI* and other future missions be able to overcome the limitations of low-resolution mass spectrometry?** *DAVINCI* VMS is based on the unit-resolution *Curiosity* SAM instrument, but the mission also includes a tunable laser spectrometer, which will provide independent measurements of key species such as $H_2O$ and CO.

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## References:

T. Gautier, J. Serigano, J. Bourgalais, S. M. Hörst, and M. G. Trainer, *Rapid Comm. Mass Spec.*, vol. 34, no. 8, 2020, doi: https://doi.org/10.1002/rcm.8684.

J. S. Greaves *et al.*, *Nat Astron*, vol. 5, no. 7, Jul. 2021, doi: 10.1038/s41550-020-1174-4.

J. H. Hoffman, R. R. Hodges, T. M. Donahue, and M. B. McElroy. *J. Geophys. Res.* **85**, 7882 (1980).

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