

INTRODUCTION: Information about the composition of biosolids such as animal wastes and manure is required to understand reactions when such materials are returned to the soil. Analytical methods which require dissolution of the sample lose information about the phosphorus containing minerals and can result in hydrolysis of organic forms. We have used Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy in conjunction with X-ray Powder Diffraction (XRPD) to quantify the amounts and forms of specific phosphorus minerals in freeze-dried or fresh animal wastes.

MAGIC ANGLE SPINNING ³¹P NUCLEAR MAGNETIC RESONANCE

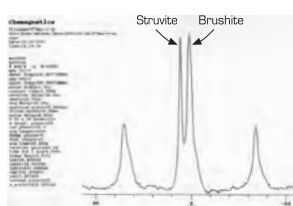
NMR spectra were obtained using a Varian/Chemagnetics CMX300 LITE instrument.



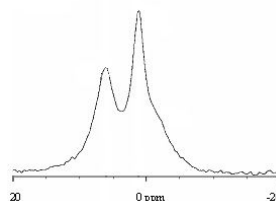
Typical parameters:

- Frequency of rotation: 6 kHz
- Time (cross-polarization)
- Excitation pulse 3.5 μs (90°)
- Recycle 4 s
- Contact 1 ms
- Number of acquisitions: > 2500

The spectrum of sheep faeces shows two main resonances, which from chemical shift positions and the pattern of sidebands, were attributable to brushite and struvite.



MAS NMR of pig faeces also indicated the presence of struvite and calcium phosphate.



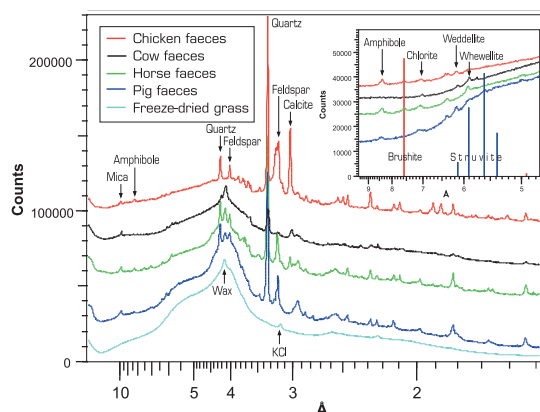
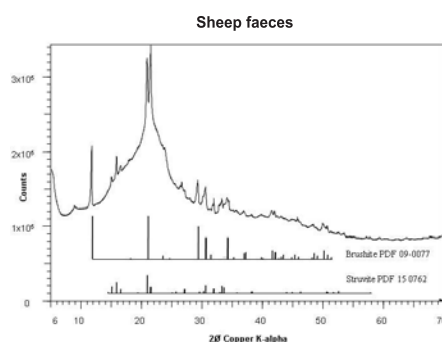
From chemical shifts alone, identification of P species is ambiguous. However, a combination of NMR and XRPD can provide definitive information.

X-RAY POWDER DIFFRACTION

Diffractograms were obtained using a Panalytical X'Pert Pro instrument.

Typical parameters:

- 25-mm diameter, 2-mm deep holder
- Radiation Cu Kα
- Scan 17.5 h
- Angle 5 and 70° (2 θ)
- Step size 0.017°
- Frequency of rotation 6 rpm



RESULTS AND DISCUSSION: Sheep faeces: The diffractogram of the sheep faeces showed the presence of brushite ($\text{Ca HPO}_4 \cdot 2\text{H}_2\text{O}$) and struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$). Quantitative analysis, performed using a reference intensity ratio method showed the sample contained 29% of the total phosphorus as struvite and 34% of the total phosphorus as brushite.

Chicken, cow, horse and pig faeces: The horse and chicken faeces showed the presence of brushite. The diffractogram from pig, cow and chicken faeces indicated the presence of whewellite (calcium oxalate monohydrate) and weddellite (calcium oxalate dihydrate). The samples also contained soil minerals (quartz, mica and amphibole). The chicken faeces contained calcite, most likely from oyster shell in the diet.

Freeze-dried grass: The diffractogram of freeze-dried grass showed a broad peak with a signal that was attributable to wax.

CONCLUSION: ³¹P MAS NMR spectroscopy in conjunction with XRPD provides information about the amounts and forms of specific phosphorus minerals in biosolids.