

# Calibration method at the N *K*-edge using interstitial nitrogen gas in solid-state nitrogen-containing inorganic compounds

Adam W. Gillespie,<sup>a\*</sup> Fran L. Walley,<sup>a</sup> Richard E. Farrell,<sup>a</sup> Tom Z. Regier<sup>b</sup> and Robert I. R. Blyth<sup>b</sup>

<sup>a</sup>Department of Soil Science, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 5A8, and

<sup>b</sup>Canadian Light Source Inc., University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0X4.

E-mail: adam.gillespie@usask.ca

The standard method of soft X-ray beamline calibration at the N *K*-edge uses the  $\nu = 0$  peak transition of gas-phase N<sub>2</sub>. Interstitial N<sub>2</sub> gas trapped or formed within widely available solid-state ammonium- and amine-containing salts can be used for this purpose, bypassing gas-phase measurements. Evidence from non-nitrogen-containing compounds (KH<sub>2</sub>PO<sub>4</sub>) and from He-purged ammonium salts suggest that production of N<sub>2</sub> gas is through beam-induced decomposition. Compounds with nitrate or nitrite as anions produce coincident features and are not suitable for this calibration method.

© 2008 International Union of Crystallography  
Printed in Singapore – all rights reserved

**Keywords:** XANES; NEXAFS; calibration; nitrogen; *K*-edge; ammonium; sulfate; phosphate; chloride; nitrate; nitrite; hydroxylamine.

## 1. Introduction

The ideal method for energy calibration of soft X-ray analysis at the nitrogen *K*-edge is the measurement of the vibrational peak positions of gas-phase N<sub>2</sub> with an in-line mounted gas cell. The vibrational manifold of the  $1s \rightarrow \pi^*$  transition is well known from electron spectroscopy, and the  $\nu = 0$  peak has an energy of 400.8 eV (Sodhi & Brion, 1984; Schwarzkopf *et al.*, 1999). Not all beamlines have facilities for gas-phase measurements, however, and in beam-time shifts where solid-state measurements are planned, set-up and use of the gas cell can be unwieldy and time-consuming.

Characteristic N<sub>2</sub> molecular vibrations in nitrogen-containing salts were observed during an investigation of natural reference compounds (Leinweber *et al.*, 2007). Also, trapped N<sub>2</sub> gas has been reported in the characterization of N<sub>2</sub><sup>+</sup>-bombarded alumina (Holgado *et al.*, 2003), and of compound semiconductors (Petravic *et al.*, 2006; Ruck *et al.*, 2004). The objective of this study was to conduct an assessment of suitable inorganic compounds that can be used for a simple alternative calibration method at the N *K*-edge using high-resolution scans over energies corresponding to N<sub>2</sub> gas.

## 2. Materials and methods

### 2.1. Reference compounds

The inorganic N-containing salts used as reference compounds are listed in Table 1. All reference compounds were pulverized with a mortar and pestle, affixed to double-sided conductive carbon tape (SGE, Toronto, Ontario, Canada) and mounted onto stainless steel sample discs. In addition, hydroxylamine hydrochloride and ammonium sulfate were dissolved in deionized water, purged with ultra-high-purity helium, evaporated under helium to remove existing N<sub>2</sub> gas, and pulverized and mounted as described above. Gas-phase photoabsorption N<sub>2</sub> measurements were obtained using a double

ionization gas cell with a 10 cm active pathlength in each chamber (Yates *et al.*, 2000) for comparison with N<sub>2</sub> vibrations measured in solid-state samples.

### 2.2. N *K*-edge XANES

Nitrogen *K*-edge X-ray absorption near-edge structure (XANES) spectra were collected using the spherical grating monochromator beamline 11ID-1 at the Canadian Light Source, Saskatoon, Saskatchewan, Canada. This facility delivers 10<sup>11</sup> photons s<sup>-1</sup> at the N *K*-edge with a resolving power ( $E/\Delta E$ ) greater than 10000 (Regier, Krochak *et al.*, 2007; Regier, Paulsen *et al.*, 2007). Fluorescence yield (FLY) data were recorded using a two-stage multichannel plate detector that was operated in parallel with total electron yield (TEY) data collection through measurement of the drain current from the sample. High-resolution scans were taken using a step size of 0.01 eV over the expected range for N<sub>2</sub> gas, and of 0.1 eV for the remainder of the scan. Spectra were normalized to the incident flux using an in-line Au mesh which was refreshed by evaporation *in situ* prior to data

**Table 1**

Names, formulae, CAS (Chemical Abstracts Service) numbers and suppliers for compounds used in this study.

Compound	Formula	CAS number	Supplier
Ammonium chloride	NH <sub>4</sub> Cl	12125-02-9	AnalaR
Ammonium phosphate, dibasic	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	7783-28-0	BDH
Ammonium phosphate, monobasic	(NH <sub>4</sub> )H <sub>2</sub> PO <sub>4</sub>	7722-76-1	EMD
Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	7783-20-2	Fisher
Ammonium nitrate	NH <sub>4</sub> NO <sub>3</sub>	6484-52-2	Sigma-Aldrich
Hydroxylamine hydrochloride	NH <sub>2</sub> OH.HCl	5470-11-1	Chemservice
Potassium nitrate	KNO <sub>3</sub>	7757-79-1	EMD
Sodium nitrite	NaNO <sub>2</sub>	7632-00-0	Sigma-Aldrich
Potassium dihydrogen phosphate†	KH <sub>2</sub> PO <sub>4</sub>	7778-77-0	Baker

† Ultra-high purity (99.8%).

collection. Data processing was carried out using the *Athena* software package (version 0.8.050). Data from at least two scans were averaged, and background-corrected by a linear regression fit through the pre-edge region followed by normalization to an edge step of unity.

### 3. Results and discussion

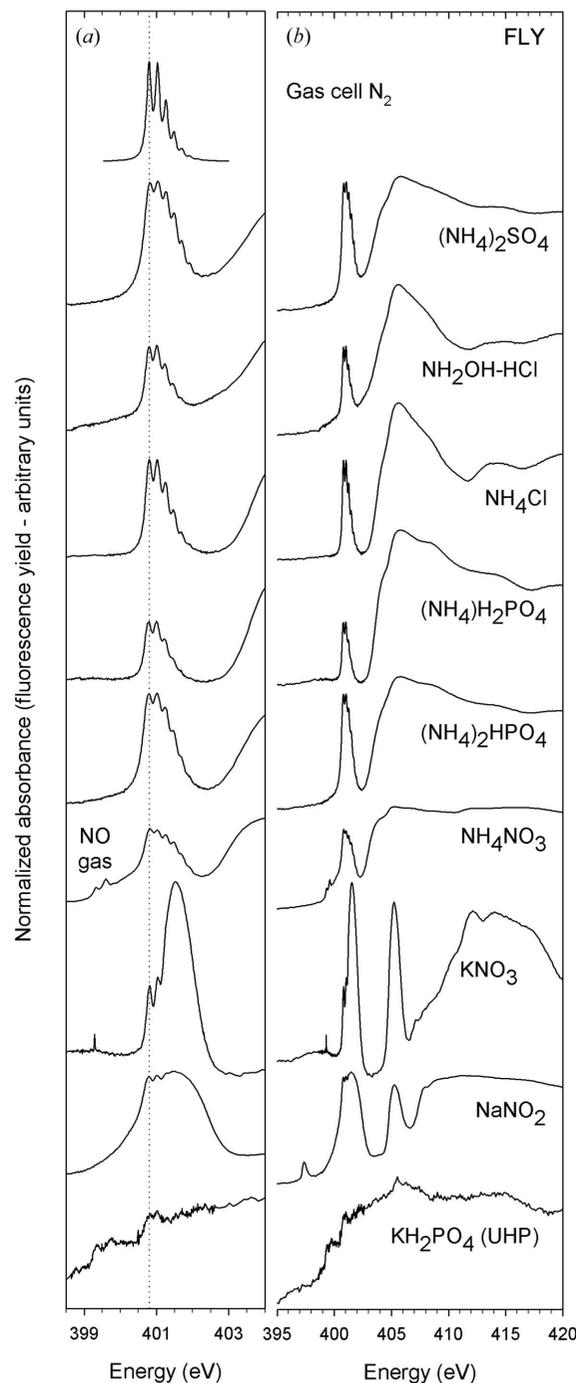
Fig. 1 shows FLY data of N *K*-edge XANES scans for the inorganic N-containing compounds studied, with panel (a) illustrating the energy region surrounding the vibronic structure of N<sub>2</sub> gas in detail, and panel (b) showing the full scan. Nitrogen gas vibronic structure is clearly evident in the reduced N-containing (*i.e.* ammonium- or amine-containing) salts that do not have an oxidized N anion. The  $\nu = 0$  transition occurs at the same peak position in the solid phase as it does in the gas phase (Fig. 1a). The data of Chen & Sette (1989) show no significant shift in the peak position until the peak width broadens by over 100 meV, by which time a significant change in the overall shape has occurred. Provided there is a valley between the second and third peaks, we quantitatively estimate the accuracy to be within 100 meV. Peak widths, however, vary owing to lifetime reduction through solid-state mechanisms. This change correlates with the crystal lattice constant, and thus with confinement of N<sub>2</sub> gas within the solid phase. This has been discussed in detail with respect to compound semiconductors by Petravic *et al.* (2006).

The presence of nitrate (NO<sub>3</sub>) or nitrite (NO<sub>2</sub>) produces a feature at 401.7 eV, which is coincident with  $1s \rightarrow \pi^*$  of N<sub>2</sub> gas, rendering these compounds less useful for calibration purposes. Although observed previously (Leinweber *et al.*, 2007), this feature remains unidentified. It should be noted, however, that this feature was not observed in previously published analyses of KNO<sub>3</sub> (Vinogradov & Akimov, 1998; Rodrigues *et al.*, 2007), suggesting that it may be a product of beam-induced decomposition. If this is the case, it is not likely to be decomposing to nitrous oxide (N<sub>2</sub>O) or nitrogen dioxide (NO<sub>2</sub>), as this feature does not match previously published spectra for these oxides of N (Gejo *et al.*, 2003; Adachi & Kosugi, 1995). Decomposition to NO, however, is observed here in NH<sub>4</sub>NO<sub>3</sub>, with vibrations corresponding to published results (Adachi & Kosugi, 1995; Yates *et al.*, 2000; Remmers *et al.*, 1993).

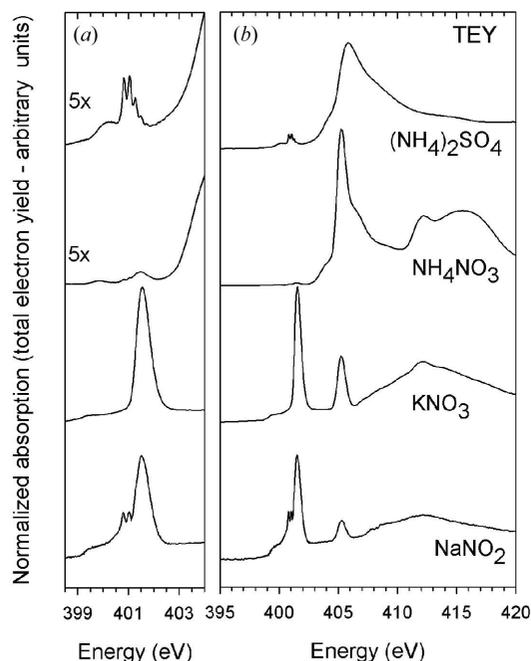
Certainly, atmospheric N<sub>2</sub> trapped within the solid phase would explain the occurrence of this feature, implying that the use of any inorganic salt would suffice as a calibration material. However, spectra obtained for N-free ultrapure potassium phosphate (dibasic) showed no evidence of N<sub>2</sub> gas vibrational structure (Fig. 1). In addition, we analyzed ammonium sulfate and hydroxylamine hydrochloride that had been dissolved, purged of N<sub>2</sub> and recrystallized under an ultra-high-purity helium atmosphere. These scans showed the presence of N<sub>2</sub> gas, matching those obtained for the unprocessed salts (data not shown). While it is beyond the scope of this paper to determine the mechanism of entrapment or production of interstitial N<sub>2</sub>, these results suggest that it is derived from decomposition of the ammonium moiety. Indeed, for calibration purposes, the salt must contain ammonium- or amine-N to be of use.

TEY spectra for selected scans are shown in Fig. 2, with panel (a) illustrating the region encompassing N<sub>2</sub> gas within the full scan pictured in panel (b). Scans for all the ammonium-containing salts, except NH<sub>4</sub>NO<sub>3</sub>, showed similar characteristics; thus only data for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> are presented here as a representative scan. The N<sub>2</sub> gas vibronic feature is suppressed in all TEY scans for all substances, and is absent from NH<sub>4</sub>NO<sub>3</sub> and KNO<sub>3</sub>. TEY (with an estimated penetration depth of <10 nm) is more surface sensitive than FLY (with an estimated penetration depth of 70–100 nm) (Frazer *et al.*, 2003;

Katsikini *et al.*, 1997). This suggests that the N<sub>2</sub> gas originates (*i.e.* is entrapped or produced) below the surface layer, and that any N<sub>2</sub> at/near the surface is removed in the vacuum chamber. Therefore, as a calibration method, TEY provides a less useful measure of absorption when compared with FLY. TEY data also revealed a stronger feature at 401.7 eV seen in KNO<sub>3</sub> and NaNO<sub>2</sub>, indicating that, if this is a decomposition product, the mechanism of its formation is surface-sensitive.



**Figure 1** Nitrogen *K*-edge FLY spectra showing N<sub>2</sub> gas in the solid state of inorganic salts used in this study. (a) Detail of the high-resolution section, (b) full N *K*-edge scan. The dotted line corresponds to 400.8 eV, which is the  $\nu = 0$  peak for the vibrational manifold of the  $1s \rightarrow \pi^*$  transition for N<sub>2</sub> gas (Sodhi & Brion, 1984; Schwarzkopf *et al.*, 1999).



**Figure 2**  
Nitrogen *K*-edge TEY spectra showing suppressed  $N_2$  gas detection. (a) Detail of the high-resolution section, (b) full N *K*-edge scan. The spectrum for ammonium sulfate is representative of all spectra of ammonium- and amine-containing salts.

#### 4. Conclusions

Interstitial  $N_2$  gas contained within solid-state inorganic ammonium- and amine-containing salts can be used to quickly and accurately calibrate soft X-ray beamlines at the N *K*-edge without the need for gas-cell measurements. Dinitrogen gas contained within these solids may be generated *via* beam-induced decomposition. Other, as yet unknown, compounds may be produced if the anion is an oxidized N moiety such as nitrate or nitrite. Characteristic  $N_2$  molecular features are observed more strongly with FLY, indicating formation/presence within the bulk material.

This work was supported by the Natural Sciences and Engineering Research Council (NSERC) and industrial and government partners, through the Green Crop Networks (GCN) Research Network. XANES analyses were performed at the Canadian Light Source facility, a national scientific user facility supported by the Natural Sciences and Engineering Research Council, National Research Council, the Canadian Institutes of Health Research and other federal government agencies.

#### References

- Adachi, J. I. & Kosugi, N. (1995). *J. Chem. Phys.* **102**, 7369–7376.  
 Chen, C. T. & Sette, F. (1989). *Rev. Sci. Instrum.* **60**, 1616–1621.  
 Frazer, B. H., Gilbert, B., Sonderegger, B. R. & De Stasio, G. (2003). *Surf. Sci.* **537**, 161–167.  
 Gejo, T., Takata, Y., Hatsui, T., Nagasono, M., Oji, H., Kosugi, N. & Shigemasa, E. (2003). *Chem. Phys.* **289**, 15–29.  
 Holgado, J. P., Yubero, F., Cordon, A., Gracia, F., Gonzalez-Elipe, A. R. & Avila, J. (2003). *Solid State Commun.* **128**, 235–238.  
 Katsikini, M., Paloura, E. C., FieberErdmann, M., Kalomiros, J., Moustakas, T. D., Amano, H. & Akasaki, I. (1997). *Phys. Rev. B*, **56**, 13380–13386.  
 Leinweber, P., Kruse, J., Walley, F. L., Gillespie, A., Eckhardt, K.-U., Blyth, R. & Regier, T. (2007). *J. Synchrotron Rad.* **14**, 500–511.  
 Petravic, M., Gao, Q., Llewellyn, D., Deenapanray, P. N. K., Macdonald, D. & Crotti, C. (2006). *Chem. Phys. Lett.* **425**, 262–266.  
 Regier, T., Krochak, J., Sham, T. K., Hu, Y. F., Thompson, J. & Blyth, R. I. R. (2007). *Nucl. Instrum. Methods Phys. Res. A*, **582**, 93–95.  
 Regier, T., Paulsen, J., Wright, G., Coulthard, I., Tan, K., Sham, T. K. & Blyth, R. I. R. (2007). *AIP Conf. Proc.* **879**, 473–476.  
 Remmers, G., Domke, M., Puschmann, A., Mandel, T., Kaindl, G., Hudson, E. & Shirley, D. A. (1993). *Chem. Phys. Lett.* **214**, 241–249.  
 Rodrigues, F., do Nascimento, G. M. & Santos, P. S. (2007). *J. Electron Spectrosc. Relat. Phenom.* **155**, 148–154.  
 Ruck, B. J., Koo, A., Lanke, U. D., Budde, F., Granville, S., Trodahl, H. J., Bittar, A., Metson, J. B., Kennedy, V. J. & Markwitz, A. (2004). *Phys. Rev. B*, **70**, 235202.  
 Schwarzkopf, O., Borchert, M., Eggenstein, F., Flechsig, U., Kalus, C., Lammert, H., Menthel, U., Pietsch, M., Reichardt, G., Rotter, P., Senf, F., Zeschke, T. & Peatman, W. B. (1999). *J. Electron Spectrosc. Relat. Phenom.* **103**, 997–1001.  
 Sodhi, R. N. S. & Brion, C. E. (1984). *J. Electron Spectrosc. Relat. Phenom.* **34**, 363–372.  
 Vinogradov, A. S. & Akimov, V. N. (1998). *Opt. Spectrosc.* **85**, 53–59.  
 Yates, B. W., Hu, Y. F., Tan, K. H., Retzlaff, G., Cavell, R. G., Sham, T. K. & Bancroft, G. M. (2000). *J. Synchrotron Rad.* **7**, 296–300.