Chemical profiling of explosives

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Chapter 6

Isotopic and elemental profiling of ammonium nitrate in forensic explosives investigations

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Abstract

Ammonium nitrate (AN) is frequently encountered as explosive in forensic casework. It is widely available as fertilizer and easy to implement in explosive devices, for example by mixing with a fuel. Forensic profiling methods to determine whether material found on a crime scene and material retrieved from a suspect arise from the same source are becoming increasingly important. In this chapter, we have explored the possibility of using isotopic and elemental profiling to discriminate between different batches of AN. Variations within a production batch, between different batches from the same manufacturer, and between batches from different manufacturers were studied using a total of 103 samples from 19 different fertilizer manufacturers. Isotope-ratio mass spectrometry (IRMS) was used to analyze AN samples for their $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope ratios. The trace-elemental composition of these samples was studied using inductively coupled plasma–mass spectrometry (ICP–MS). All samples were analyzed for the occurrence of 66 elements. 32 of these elements were useful for the differentiation of AN samples. These include magnesium (Mg), calcium (Ca), iron (Fe) and strontium (Sr). Samples with a similar elemental profile may be differentiated based on their isotopic composition. Linear discriminant analysis (LDA) was used to calculate likelihood ratios and demonstrated the power of combining elemental and isotopic profiling for discrimination between different sources of AN.
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6.1 Introduction

Ammonium nitrate (AN) has applications as explosive in industry, such as mining and civil construction [1,2]. Its chemical stability and low sensitivity to shock and friction [1,3,4] make it relatively safe to produce and to handle in large quantities. Combined with its low costs these properties make AN a suitable explosive. Explosive-grade ammonium nitrate generally exists in the form of slurries, emulsions, or porous prills mixed with a fuel (ammonium nitrate fuel oil, ANFO) [1]. Obtaining explosive-grade AN for criminal abuse is difficult due to extensive regulations, but AN in the form of fertilizer prills or granules is widely available [1,3,4]. The European Commission prohibits the distribution of ammonium nitrate-containing fertilizers with a nitrogen percentage higher than 16% to private parties [5]. In addition, detonation tests should be performed on fertilizers with a nitrogen content of more than 28% [6]. Fertilizer prills have a higher density and a lower porosity than explosive-grade prills, reducing the sensitivity to detonate. However, fertilizer-grade ammonium nitrate can still detonate or be made to detonate [3,4]. Examples of attacks involving fertilizer-based explosive devices are the bombings in Oklahoma City in 1995 and Oslo in 2011.

In case of criminal use in an improvised explosive device (IED), chemical profiling of AN is an important tool to investigate the origin of the material used. In this work, we will examine the possibility of establishing relationships between AN retrieved from an IED and AN associated with a suspect. We will also investigate the possibility of tracing ammonium nitrate back to its production location. Product classification can yield important information especially for intelligence purposes and in the absence of leads and suspects. Chemical profiling of AN is especially challenging because of its inorganic nature and the bulk quantities in which it is produced. In this work the potential of profiling based on trace-elemental composition and isotope ratios has been investigated.

Ammonium nitrate is manufactured from ammonia and nitric acid [1,4,7]. Ammonia production occurs through the reaction of hydrogen with atmospheric nitrogen according
to the Haber process [8]. Thereafter, nitric acid is formed by the oxidation of ammonia (the Ostwald process) [1,4,8]. Both the nitrogen and oxygen in ammonium nitrate are retrieved from the atmosphere. Although there is not much variation in the isotopic composition of atmospheric nitrogen and oxygen around the world [9], fractionation can occur during AN synthesis resulting in variation in both $\delta^{15}N$ and $\delta^{18}O$ values for different samples. Fertilizer prills or granules consist, besides ammonium nitrate, of various additives, such as gypsum, dolomite and magnesium nitrate. In addition, the prills are coated with a water-repellent material to prevent the prills from absorbing water [1-4,10]. These additives also contribute to the isotopic signature of the prills/granules. Moreover, the additives used during the manufacturing of AN-based fertilizers are rich in elements and therefore determine the elemental composition of the fertilizer prills. Two techniques that are, therefore, of special interest for profiling AN are isotope-ratio mass spectrometry (IRMS) and inductively-coupled plasma–mass spectrometry (ICP–MS). As part of the ICP–MS study also the application of laser-ablation ICP–MS (LA–ICP–MS) was investigated for element profiling of individual granules or prills. LA–ICP–MS could provide profiling options in forensic post explosion investigations where only a limited number of granules or prills are found.

6.1.1 Forensic applications of IRMS and ICP–MS.

Most of the analytical techniques conventionally used in forensic science are not able to determine whether samples with the same chemical identity have a common source. IRMS can in principle be used to study the source of samples based on their isotopic composition. In the field of explosives, IRMS was previously used to discriminate between different sources of Semtex [11], triacetone triperoxide (TATP) [12], pentaerythritol tetranitrate (PETN) [12,13], black powder, flash powder, nitromethane, plastic explosive no. 4 (PE4) [14], trinitrotoluene (TNT) [13-15], urea nitrate [16], and ammonium nitrate [13,17]. With one exception [17] these were all preliminary studies with either a small sample set or limited information on the origin of the materials. In addition to the ability to examine the source of explosive samples, IRMS has also been used to study relationships between precursors and the explosive product for urea nitrate [16], cyclotrimethylenetrinitramine (RDX) [18] and hexamethylene triperoxide
diamine (HMTD) as described in chapter 5. Benson et al. [17] attempted to correlate the isotopic composition of post-explosion AN to the isotopic composition of the intact AN, but without success. Therefore, we did not consider the analysis of post-explosion AN residues in the present project. In addition, we did not consider explosive mixtures of AN (e.g. with a fuel or sugar), because this requires isolation of the AN from the mixture.

ICP–MS is capable of detecting and quantifying multiple elements and thus of producing trace-elemental signatures. Samples can be introduced in the plasma either by nebulization (liquids or solutions) or by laser ablation (LA–ICP–MS). When sufficient evidence material is available spraying from solution will provide the most accurate quantitative analysis as it allows for homogenization of the material. However, the use of laser ablation allows for trace-element profiling of small amounts of material and for studying the spatial distribution of the trace elements (2D and 3D profiling). Elemental profiles obtained using ICP–MS have been used to discriminate between different sources of glass [19-21], paint [22], tapes [23], white cotton fibers [24], beer [25], bullets [26], methylamphetamine [27], human bones and teeth [28], and in the detection of art forgeries [29]. The combination of IRMS and ICP–MS may result in complementary information on the origin of a material and has shown to be powerful in discriminating between different sources of document paper [30].

6.1.2 Challenges of IRMS for nitrates

Stable-isotope analysis of nitrogen-containing samples and nitrates in particular poses some challenges. Meier-Augenstein et al. [31] reported on the influence of N$_2$ gas formed during high-temperature reduction of nitrogen-rich compounds on $\delta^2$H analysis. Partial overlap of the N$_2$ and H$_2$ peaks after GC separation resulted in inaccurate and imprecise $\delta^2$H values, either due to dilution of the H$_2$ peak or to ionization competition between H$_2$ and N$_2$ gas. Mimicking nitrogen-rich samples by adding silver nitrate to benzoic acid samples resulted in a shift of roughly 5‰ towards more negative $\delta^2$H-values for an N:H ratio of one compared to ‘nitrogen-free’ benzoic acid.
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$\delta^{18}O$ measurements are performed by conversion of elemental oxygen in the sample to carbon monoxide (CO) using high-temperature conversion (HTC) in a reactor packed with glassy carbon. The IRMS is then used to measure the amounts of m/z 28 ($^{12}\text{C}^{16}\text{O}$) and m/z 30 ($^{12}\text{C}^{18}\text{O}$) to determine $^{18}\text{O}^{16}\text{O}$ ratios in a sample. Conversion of oxygen in inorganic samples to CO has proven to be challenging. Powdered [32] or nickelized carbon [33-36] has been added either to the reactor or directly to the capsules containing the samples. Farquhar et al. [37] used a reactor packed with nickelized carbon only instead of glassy carbon. Nickel acts as a catalyst, enhancing the conversion to CO and allowing the use of lower reaction temperatures. The use of nickelized carbon resulted in more precise $\delta^{18}O$ measurements.

The hygroscopic nature of AN is another point of concern. For prills or granules, water absorption is minimized by coating with an inert, hydrophobic material [1-4,10]. However, sample preparation for IRMS requires grinding of the prills or granules, causing interaction with atmospheric water. Exchange of oxygen was not observed for KNO$_3$ and NaNO$_3$ reference materials (USGS34, IAEA-NO-3 and USGS35) [32,38]. In addition, $\delta^{18}O$ values of these dried nitrate standards were not affected by repeated sorption and desorption of H$_2$O [32]. This suggests that oxygen exchange should not be an issue for ammonium nitrate, if a suitable drying and storage procedure is used to prevent absorption of water.

During high-temperature conversion, nitrogen in a sample is converted to N$_2$, which is isobaric to CO (m/z 28). Although N$_2$ and CO can be separated using a 5-Å molecular-sieve GC column, the presence of small traces of oxygen may result in formation of NO$^+$ at the hot filament of the ion source. Whereas the signals of m/z 28 ($^{14}\text{N}_2$) and m/z 29 ($^{14}\text{N}^{15}\text{N}$) quickly diminish after elution of the N$_2$ peak, NO disappears slowly from the ion source, resulting in a long tail in the m/z-30 signal that extends into the $^{12}\text{C}^{18}\text{O}$ peak, rendering accurate $\delta^{18}O$ measurements impossible. The extent of N$_2$ interference is related to the amount of N$_2$ formed during high-temperature conversion, which in turn depends on the type of compound analyzed. Hunsinger et al. [39] demonstrated that nitrogen from nitro or nitrate groups was efficiently converted to N$_2$, whereas the
N$_2$ yield for amine/amide-containing compounds was around 65% and for caffeine the N$_2$ yield was even lower. The high nitrogen content of ammonium nitrate necessitates effective removal of the N$_2$ interferences, as suggested by Benson et al. [17].

Several approaches to eliminate or reduce the isobaric interference of N$_2$ with CO measurements have been reported. Separation of N$_2$ and CO can be improved by replacing the conventional 0.6-m GC column with a longer one, allowing more time for the m/z 30 signal to return to the baseline. However, merely extending the length of the column led to a reduction of the m/z 30 background offset, but it did not eliminate the N$_2$ interference, especially not for samples having a high nitrogen content [37,39]. Another option to reduce the interference of N$_2$ with $\delta^{18}$O measurements is to reduce the amount of N$_2$ in the ion source or to prevent N$_2$ from entering the ion source altogether. This can be achieved by installing a switching valve between the GC column and the IRMS to divert the gas stream during elution of the N$_2$ peak [32,39-41] or by diluting the N$_2$ peak with helium using the open-split interface between the GC column and the IRMS [39,40]. Qi et al. [41] observed that combining the use of a longer column with diversion of the N$_2$ peak yielded the most accurate and precise $\delta^{18}$O values. Diversion of the N$_2$ peak requires the installation of a switching valve between the elemental analyzer and the IRMS. Therefore, our approach to minimize N$_2$ interference was to combine the use of a longer column with He-dilution through the existing open-split interface. Other possible measures to reduce the interference of N$_2$ with $\delta^{18}$O measurements include application of a CO-reference-gas pulse between the N$_2$ and CO peaks [34] and improving background correction by subtracting the tail of the N$_2$ peak from the area of the CO peak [40].

### 6.2 Experimental

#### 6.2.1 Sample collection

All samples used in this work are ammonium nitrate-based fertilizers. Ammonium nitrate granules were obtained from a European fertilizer manufacturer. These samples will be designated as originating from ‘country 1’. Two different types of AN were
collected with nitrogen contents of 27% and 33.5%, respectively. These AN types are classified as ‘type A’ fertilizers because of their high nitrogen content. Therefore, they need to be tested for their detonation properties according to EU regulation nr. 2003/2003 [6]. Samples were taken during each hour of production of a single batch. All samples were taken at the end of the production process, i.e. after granulation and coating. This yielded a total 20 samples for the 27%-N granules, and 18 samples for the 33.5%-N ones. In addition, 6 different 27%-N batches were sampled, as well as 9 different 33.5%-N batches. Raw materials (coating material, dolomite and gypsum) were obtained from the same manufacturer to investigate whether elemental profiles obtained for the ammonium nitrate could be correlated with these raw materials. Furthermore, a total of 48 ‘type A’ AN samples, either in the form of granules or prills, originating from 18 different fertilizer manufacturers in 8 different countries were obtained from TNO (Rijswijk, The Netherlands). Samples were categorized as different types based on their nitrogen contents and type of additives. In total, six different types of AN were defined, with type 1 being the 27%-N AN (27 samples in total) and type 2 the 33.5%-N samples (46 samples). 13 samples could not be classified as one of the six types of AN and are therefore designated as ‘other’ in this chapter.

6.2.2 Elemental analysis

6.2.2.1 Sample preparation

All samples were prepared using acid digestion for ICP–MS analysis. To this end 3 mL of 65% nitric acid (Merck, Darmstadt, Germany) were added to 200 mg of ground AN in a 13 mL polypropylene tube with a two-position cap (Sarstedt, Nümbrecht, Germany). Digestion was performed for 2 h in a digital block heater (Grant, Cambridgeshire, UK) controlled at 90°C. After addition of 1 mL of 30% hydrogen peroxide (Merck, Darmstadt, Germany), the samples were placed in the block heater for another 2 h. A volume of 0.5 mL of a solution of 10 μg/mL rhenium in 2% HNO₃ (CPI International, Santa Rosa, CA, USA) was added as internal standard and ultrapure water, prepared using a PureLab Ultra (Elga, High Wycombe, UK) system, was added to a total volume of 10 mL. Prior to ICP–MS analysis, the samples were diluted tenfold with ultrapure water. Reference sample ISE 989 (soil) was prepared according to the same procedure for quality control.
Soil is a different matrix, but AN matrix-matched reference materials are not available. Concentrations of 66 elements (Li, Be, B, Na, Mg, Al, K, Ca, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Br, Se, Rb, Sr, Y, Zr, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, I, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th and U) were determined through 6-point calibrations in the range of 0.01–200 ppb using multi-element standards obtained from CPI International. The concentrations of Mg, Ca, Cr, Ni and Pb were corrected for low levels occurring in the procedural blanks.

6.2.2.2 Instrumental parameters ICP–MS

ICP–MS analyses were performed on a PerkinElmer (Waltham, MA, USA) Elan 6100 DRC Plus instrument, coupled to an ASX-500 autosampler (CETAC technologies; Omaha, NE, USA), from which sample solutions were introduced at a flow rate of 1 mL/min using a peristaltic pump. The instrument was operated with a Meinhard (Golden, CO, USA) quartz concentric nebulizer and a baffled quartz cyclonic spray chamber (PerkinElmer). ICP–MS settings are shown in Table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>ICP-MS</th>
<th>LA-ICP-MS</th>
<th>ICP-OES</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICP RF power</td>
<td>1325 W</td>
<td>1325 W</td>
<td>1400W</td>
</tr>
<tr>
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<td>16 L/min</td>
<td>16 L/min</td>
<td>15 L/min</td>
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<tr>
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<td>0.85 L/min</td>
<td>0.8 L/min</td>
</tr>
<tr>
<td>Auxiliary flow</td>
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<td>1.5 L/min</td>
<td>0.2 L/min</td>
</tr>
<tr>
<td>Dwell time per amu</td>
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<td>20 ms</td>
<td>-</td>
</tr>
<tr>
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<td>Peak hopping</td>
<td>Peak hopping</td>
<td>-</td>
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<tr>
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<td>3% HNO3</td>
<td>-</td>
<td>3% HNO3</td>
</tr>
<tr>
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<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Readings/replicate</td>
<td>1</td>
<td>390</td>
<td>-</td>
</tr>
<tr>
<td>Replicates</td>
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<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

6.2.2.3 Laser-ablation ICP–MS

The possibility of obtaining elemental profiles on single ammonium nitrate granules or prills was examined using laser-ablation ICP–MS (LA–ICP–MS). A New Wave
(Fremont, CA, USA) UP213 (Nd:YAG 213 nm) laser-ablation system with a SuperCell ablation chamber was used in conjunction with the ICP–MS system as described in section 6.2.2.2. Eight different AN samples with four granules/prills each were scanned for the presence of 16 elements (Li, B, Na, Mg, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba, Pb) with a dwell time of 20 ms. Samples were analyzed using both spot sampling (sampling time 25 s) and line scanning (3 mm line scans with a scan speed of 25 μm/s preceded by pre-ablation). In both cases the laser energy was set at 0.07 mJ and a spot size of 110 μm and a 10-Hz repetition rate were used. Ablated particles were transferred to the plasma using helium as carrier gas with a flow rate of 750 mL/min. AN granules and prills sampled by LA–ICP–MS were studied using a Quanta 400 scanning electron microscope (SEM) (FEI, Hillsboro, OR, USA).

6.2.2.4 ICP optical-emission spectroscopy
Concentrations of the elements that occurred at levels higher than 100 mg/kg in AN (Ca, Fe, Mg, K, Mn and Sr), were determined using a PerkinElmer Optima 5300 DV ICP optical-emission spectroscopy (ICP–OES) instrument in radial-viewing mode, equipped with an ASX-500 autosampler (CETAC technologies) from which sample solutions were introduced with a flow rate of 1.5 mL/min using a peristaltic pump. The instrument was operated with a Ryton Scott spray chamber and a cross-flow nebulizer (PerkinElmer). The digested solutions were tenfold diluted with ultrapure water. Yttrium was added to all samples and standards as internal standard at a concentration of 10 ppm. Calibration solutions were prepared at levels of 1, 5, 15, 30, 65 and 100 ppm. ICP–OES and MS results that were obtained in the overlapping linear range were in good agreement. ICP–OES results are not reported separately, but as part of the ICP–MS results.

6.2.3 IRMS stable-isotope analysis
All samples were analyzed for their nitrogen- and oxygen-isotope ratios using a Delta V Advantage IRMS with a ConFlo IV interface (both from Thermo Fisher Scientific, Bremen, Germany).
6.2.3.1 $\delta^{15}$N analysis

Samples were ground and mixed 1:1 (mass based) with powdered sugar (Van Gilse, Suiker Unie, Oud Gastel, The Netherlands) for quantitative conversion of the sample. Samples were weighed into tin capsules (3.3 $\times$ 5 mm; IVA Analysentechnik, Meerbusch, Germany) with a mass corresponding to approximately 100 $\mu$g of nitrogen and placed in a MAS 200R carousel autosampler (Thermo Fisher Scientific). Nitrogen-isotope ratios were measured from the N$_2$ gas formed utilizing a FlashEA 1112 (Thermo Fisher Scientific) elemental analyzer. Samples were combusted in a reactor (1020°C) packed with chromium oxide and cobalt oxide using an oxygen pulse of 8 s at 175 mL/min. After oxidation, sample gases were transferred to a reduction reactor (650°C) packed with copper, where NO$_x$ was reduced to N$_2$. The system was equipped with a CO$_2$-trap containing magnesium perchlorate and ascarite, and a water trap containing magnesium perchlorate. The gases were separated on a 3-m stainless-steel packed GC column (Porapak QS, ID 5 mm), held at 35°C. $\delta^{15}$N values were calibrated to the international scale using the certified reference materials IAEA-N-1 ($\delta^{15}$N 0.43 ± 0.20) and IAEA-N-2 ($\delta^{15}$N 20.41 ± 0.20) (both from IAEA, Vienna, Austria) [42]. An in-house casein standard ($\delta^{15}$N 5.94 ± 0.08) was used to monitor the analytical performance.

6.2.3.2 $\delta^{18}$O analysis

All samples and standards were ground, dried in an oven at 60°C for ca. 3 h and mixed with 50% nickelized carbon (100 $\mu$g NiC per 50 $\mu$g of oxygen in the sample; Elemental Microanalysis, Okehampton, UK). Prior to addition to the samples, the nickelized carbon was baked in the TC/EA reactor at 1400°C for at least 16h to remove any oxygen contamination. After addition of NiC the samples were dried again in an oven at 60°C and weighed into silver capsules (3.2 $\times$ 4 mm; IVA Analysentechnik) with a mass corresponding to 70 $\mu$g of oxygen. Subsequently, samples were dried overnight in a vacuum oven at 60°C, transferred to the autosampler carousel and stored in a vacuum desiccator until analysis. Conversion of sample-oxygen to CO was performed using a thermal-conversion elemental analyzer (TC/EA; Thermo Fisher Scientific). The MAS 200R autosampler was covered using a box flushed with argon to minimize atmospheric water absorption. The TC/EA reactor (maintained at 1400°C) consisted of a glassy-
carbon tube, packed with glassy-carbon chips, placed inside a ceramic (aluminum oxide) tube. A crucible was placed on top of the glassy-carbon fragments to trap the ash and remaining silver capsules. The crucible was replaced after analyzing roughly 100 samples. The TC/EA was operated in reversed-flow using a bottom-feed adapter (IVA Analysentechnik) for improved precision [43,44]. A chemical trap containing ascarite and magnesium perchlorate was installed between the reactor and the GC column. The conventional 0.6-m 5-Å molecular-sieve GC column (80–100 mesh) (Varian, Middelburg, The Netherlands) was replaced by a 1.5-m column (60–80 mesh, IVA Analysentechnik), operated at 70°C, to improve separation of the N$_2$ and CO peaks, as suggested by Qi et al. [41]. The open-split interface (Conflo IV) was set such as to apply maximum He dilution during elution of the N$_2$ peak to minimize interference of N$_2$ with the CO peak. $\delta^{18}$O values were corrected to the international VSMOW-scale using USGS34 (KNO$_3$; $\delta^{18}$O -27.78 ± 0.37‰), USGS35 (NaNO$_3$; $\delta^{18}$O +56.81 ± 0.31‰) (both from NIST, Gaithersburg, MD, USA) and IAEA-NO-3 (KNO$_3$; $\delta^{18}$O +25.32 ± 0.29‰) certified reference materials [38].

6.3 Results and discussion

6.3.1 ICP–MS

All samples were scanned for the presence of 66 elements. 32 Elements were detected in at least one of the samples, whereas 24 elements were not detected in any of the samples. Some elements were excluded from further comparisons because of analytical limitations. Br and I were not considered because of their low ionization efficiencies, Al because of observed contamination due to the use of an aluminum block heater for the acid digestion of the samples and Na and Sn because of relatively high levels in procedural blanks. Major elements detected in the AN samples included Ca, Fe, Mg, K, Mn and Sr. In several samples these elements were present at levels higher than 200 ppb in solution (or 100 mg/kg in AN), which was outside the calibration range of the ICP–MS instrument. The concentrations of these elements were conveniently determined using ICP–OES, which exhibits a broad linear range.
Table 6.2. Levels of elements detected in two different types of AN from a single manufacturer. The average concentration per element is given in mg/kg AN. Samples originating from a single batch were sampled every hour during the production process. Samples from different batches were manufactured within a period of 9 months.

<table>
<thead>
<tr>
<th>Element</th>
<th>Type 1 (27% N)</th>
<th>Type 2 (33.5% N)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Control sample</td>
<td>Same batch</td>
</tr>
<tr>
<td></td>
<td>(n = 9)</td>
<td>(n = 20)</td>
</tr>
<tr>
<td></td>
<td>mg/kg</td>
<td>CV (%)</td>
</tr>
<tr>
<td>Li</td>
<td>1.87</td>
<td>3.6</td>
</tr>
<tr>
<td>B</td>
<td>9.1</td>
<td>6.3</td>
</tr>
<tr>
<td>Mg</td>
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<td>3.1</td>
</tr>
<tr>
<td>K</td>
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</tr>
<tr>
<td>Ca</td>
<td>51400</td>
<td>1.7</td>
</tr>
<tr>
<td>Sc</td>
<td>0.11</td>
<td>22</td>
</tr>
<tr>
<td>V</td>
<td>0.35</td>
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<tr>
<td>Cr</td>
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<tr>
<td>Fe</td>
<td>450</td>
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</tr>
<tr>
<td>Co</td>
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<tr>
<td>Ni</td>
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<tr>
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<tr>
<td>Sr</td>
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<tr>
<td>Y</td>
<td>0.18</td>
<td>3.3</td>
</tr>
<tr>
<td>Zr</td>
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</tr>
<tr>
<td>Ba</td>
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<td>8.4</td>
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<tr>
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<td>31</td>
</tr>
<tr>
<td>Th</td>
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<td>17</td>
</tr>
<tr>
<td>U</td>
<td>0.04</td>
<td>18</td>
</tr>
</tbody>
</table>

\(^1\) Removal of one outlier with a Cu level of 5.58 mg/kg.
6.3.1.1 Samples from a single manufacturer

One of the type-1 samples (27% N) obtained from the European manufacturer (country 1) was used to monitor the repeatability of the procedure for elemental analysis. This sample was co-digested with each digestion series and analyzed together with each series. A total of 9 analyses were performed on this sample over a period of 6 months. 26 elements were detected in this control sample at levels ranging from 0.03 mg/kg (Th) to 51400 mg/kg (Ca) in AN (Table 6.2). Coefficients of variation (CV) were below 10% for 16 elements and between 10 and 20% for 8 elements. Quantitation of Sc (22%) and Pb (31%) was less consistent.

The variations in elemental composition within the type-1 batch that was sampled every hour during the production process were comparable to the within-sample variations (repeatability of the control sample). In addition, the 5 other type-1 batches exhibited comparable elemental profiles. Type-2 AN from the same manufacturer shows an elemental profile different from that of type 1, with on average lower levels of all elements. 19 elements were detected in type-2 AN, the major ones being Ca, Mg and Fe. The differences in levels of elements between type-1 and type-2 AN can be explained by their AN content. Type-2 AN has a higher AN percentage (33.5% N corresponds to 95.7% AN) compared to type-1 AN (27% N corresponds to 77.1% AN) and, therefore, smaller amounts of additives that contribute to the elemental profile. Concentrations of several elements present at low levels in type-2 AN (Li, B, Cu, Ba and Pb) showed large within-batch and between-batch variations (CV > 20%).

In addition to AN granules, raw materials, including gypsum, dolomite and coating material, were analyzed for the presence of trace elements. Gypsum (calcium sulfate) is the main additive in type-1 AN, whereas dolomite (calcium magnesium carbonate) is used as a filler for type-2 AN. In addition to Ca, gypsum was found to contain high levels (> 10 mg/kg) of Li, B, Mg, K, Mn, Fe, Zn, Sr and Ba and trace levels of V, Cr, Ni, Cu and Rb. Considering the amount of gypsum used in type-1 AN, levels of Li and B in gypsum were consistent with the levels as detected in type-1 AN. Concentrations of the elements Ca, Mn, Ni, Zn and Ba in gypsum correspond to ca. 70%, and Sr to ca. 90%,
of the concentrations of these elements in type-1 AN, indicating an additional source for these elements. Dolomite was observed to be rich in the elements Mg, K, Ca, Mn, Fe, Ni, and Zn.

6.3.1.2 Samples from different manufacturers

Substantial variations were observed in the elemental profiles of AN samples originating from different manufacturers. The elemental composition was found to depend both on the type of AN and on the production location. An example is given in Fig. 6.1 for the elements B, Mn, Zn, Ba and Pb. In general, lower levels of elements were detected in type-2 AN than in other types of AN.

![Fig. 6.1. Typical elemental profiles for AN samples with different origin. Manufacturer A from country 1 is the European manufacturer that provided the samples as discussed in section 6.3.1.1. Error bars represent inter-batch variability (1σ).](image)

The correlations between the elements that were detected in the AN samples are shown in Fig. 6.2. A high correlation is observed for the lanthanides. In many samples, these were either absent or present at very low levels, while in other samples, all lanthanides were detected. For example, AN samples from country 9 (3 manufacturers) showed higher levels of the lanthanides (La, Ce, Pr, Nd and Sm) compared to other countries. Other highly correlated elements are Ca and Sr, which for type-1 and type-2 AN from manufacturer 1 both originate from the additives, and Fe, Co and Ni. Although Sc, Rb, Ga, and Th are correlated with several other elements, these elements were not detected
Fig. 6.2. Correlation coefficients for the elements as detected in the AN samples.

These elements have not been detected in at least 40% of the samples and, therefore, their correlations should be considered carefully.
in at least 40 of the 102 samples. The large number of zero’s results in non-informative correlations.

A low number of anticorrelated elements (16 of the 496 possible combinations) were observed, all with correlation coefficients close to zero. This means that in general the concentrations of all elements increase (or decrease) for one sample compared to another, instead of one element being higher in concentration and another element having a lower concentration. This supports the hypothesis that the elements in AN mainly originate from the additives and that the elemental profiles depend on the AN content and type of additives used. Larger amounts of additives are used in samples with relatively low nitrogen content, resulting in higher concentrations for the majority of elements.

Principal component analysis (PCA) on the elemental profiles of the AN samples (after normalization of the data and removal of two outliers) showed grouping of the country-1 samples according to their type (Fig. 6.3) The type-2 AN from this manufacturer has a similar elemental composition as type-4 and type-6 AN. Several type-2 AN samples originating from other production locations are not correlated to the type-2 AN samples from country 1. A possible explanation might be the use of different additives resulting in variations in the elemental composition of AN. Type-1 AN has the lowest nitrogen content and type 6 the highest. Type-3 AN fertilizers are all sulfur-containing samples, with different nitrogen contents and different concentrations of additives.
Fig. 6.3. PCA-score plot based on 32 elements for AN samples from different production locations. PC1 is responsible for 49.7% of the total variance in the dataset and is predominantly composed of the elements Sc, Co, Fe, Ca, Li, Ga and the lanthanides. PC2 is responsible for 14.1% of the total variance and is mainly characterized by Sr and Mg.

Fig. 6.4. LA–ICP–MS line-scan profile of a type-2 AN granule. The color plot shows the intensities for each element (from top to bottom: Pb, Ba, Sr, Zn, Cu, Ni, Fe, Mn, Cr, V, Ca, K, Mg, Na, B, Li). High intensities are shown in white, low intensities in blue.
6.3.1.3 Laser-ablation ICP–MS

In cases in which a limited number of AN granules or prills is found (e.g. residues at a location, material found on clothing of a suspect or at a post-explosion scene), there may not be enough material to prepare for solution ICP–MS. In such cases elemental profiles might still be obtained by laser-ablation ICP–MS (LA–ICP–MS). LA–ICP–MS has the advantage of virtually no sample preparation and it requires minimal amounts of sample. The possibility of using LA–ICP–MS to analyze single ammonium nitrate granules/prills was examined for eight different samples. Elemental profiles were constructed based on the average signal intensity (in counts per second). The elements detected using LA–ICP–MS were in agreement with the elements observed using solution ICP–MS for the respective samples. Using spot sampling, variations both within a single granule and between different granules of the same sample were typically in the order of 60% CV. Therefore, line scans were performed to sample larger areas of the granules and to average out possible inhomogeneity effects. Although line scans were more repeatable (~30% CV) compared to spot sampling, sample heterogeneity was still an issue. Scan profiles of single granules showed substantial variation in signal intensity and positions where the concentrations of elements suddenly strongly increased (Fig. 6.4). The heterogeneity of AN granules was confirmed using scanning electron microscopy (Fig. 6.5). This study shows that the options for chemical profiling of single

Fig. 6.5. SEM images of (a) a type-1 AN granule after LA–ICP–MS analysis (spot sampling) and (b) a type-2 AN granule after both spot sampling and line scanning (circular shape).
AN granules or prills and AN-related micro traces are unfortunately limited. It is therefore advised to apply ICP–MS using the solution method, if limited AN material is available for analysis. A micro-volume sample-introduction setup as available for some of the latest ICP–MS instruments could be very useful. This will allow maximum element concentrations by digesting and dissolving samples in a minimum of solvent volume. It should be noted that the inhomogeneity of the sample may play a role when reducing the amount of sample used for digestion and ICP analysis.

6.3.2  IRMS

The fertilizer granules and prills examined in this work consisted of ammonium nitrate and additives such as dolomite, gypsum and organic coating material. Initial IRMS experiments showed that the carbon content was too low to analyze the ammonium nitrate samples for $\delta^{13}$C isotope ratios. We also attempted to determine $\delta^2$H ratios in AN samples, but we observed a similar influence of nitrogen on the $\delta^2$H measurements as reported by Meier-Augenstein et al. [31]. AN entails the additional risk of hydrogen exchange of the ammonium ion with atmospheric water. Therefore, we concluded that accurate and precise determination of $\delta^2$H ratios in ammonium nitrate was not feasible and we focused the present research on the determination of nitrogen and oxygen isotopes in ammonium nitrate samples.

6.3.2.1  $\delta^{15}$N method development

Initial experiments showed good repeatability for IAEA-N-1 and IAEA-N-2 ammonium sulfate standards. However, analyzing nitrates resulted in inconsistent $\delta^{15}$N values and gradually increasing peak widths (Fig. 6.6a and 6.6b). In addition, ammonium nitrate was not quantitatively converted to N$_2$ (Fig. 6.6c). Ammonium sulfate replicates measured after nitrate samples showed an apparent memory effect, with the first replicate showing a yield exceeding 100% and an increased peak width, returning gradually to normal peak widths and approximately 100% yield after several replicates. These results indicate that conversion of nitrates to N$_2$ is problematic. Nitrate-nitrogen differs from ammonium-nitrogen in that nitrate-nitrogen is in its highest oxidation state. Combustion in an oxygen-rich environment will therefore not yield N$_2$, but mainly NO$_x$. It is likely
that reduction of these large amounts of NO\textsubscript{x} to N\textsubscript{2} will be difficult, resulting in slow and incomplete conversion, which in turn will be reflected in smaller and tailing N\textsubscript{2} peaks.

We tested oxygen pulses with different flow rates (175 mL/min and 250 mL/min). The conversion of ammonium sulfate was not affected by the O\textsubscript{2} flow rate, but compared to ammonium sulfate, the conversion of potassium nitrate was 94% and 89% respectively. Reduced conversion of nitrates in the presence of a larger volume of oxygen supports the hypothesis that the large volumes of NO\textsubscript{x} cannot be completely reduced to N\textsubscript{2} in the reduction reactor. These observations are in agreement with the results published by Gentile et al. [45].

Fig. 6.6. Memory effect of ammonium nitrate on ammonium sulfate standards (IAEA-N-1 and IAEA-N-2), resulting in inconsistent $\delta^{15}$N values (a), increasing peak width (b) and lower conversion for AN compared to ammonium sulfate (c).
Improving the conversion of nitrates to N\(_2\) can be achieved by the addition of carbon in the form of activated charcoal [16] or sucrose [46]. The excess of carbon would result in CO\(_2\) formation, reducing the NO\(_x\) in the combustion reactor and thus enabling complete reduction to N\(_2\) by elemental copper. We have examined the efficiency of graphite and powdered sugar as carbon sources by analyzing six replicates of both ammonium sulfate standards (IAEA-N-1 and IAEA-N-2), followed by six replicates of both types of AN (27% N and 35% N) and again six replicates of both ammonium sulfate standards. This was done without any additives, with addition of graphite in a 1:1 mass ratio and with powdered sugar 1:1.

![Graph](image.png)

**Fig. 6.7.** Conversion of ammonium nitrate normalized to IAEA-N-1 without additive and with the addition of sugar or graphite.

The ‘memory effect’ that was observed (Fig. 6.6) when analyzing ammonium sulfate replicates directly after nitrate samples was not observed when graphite or sugar was added. The addition of sugar resulted in consistent and roughly identical N\(_2\) peak widths for both ammonium sulfate and ammonium nitrate and repeatable \(\delta^{15}\)N values (1 standard deviation \(\sigma\) of 0.02–0.06‰). The addition of graphite still showed slightly broader peaks for nitrates compared to ammonium sulfate and the repeatability of \(\delta^{15}\)N values was between 0.07‰ and 0.18‰ (1\(\sigma\)). Moreover, the addition of sugar resulted in efficient combustion of ammonium nitrate (Fig. 6.7), whereas graphite did not yield complete conversion to N\(_2\). Therefore, all ammonium nitrate samples were analyzed for
their nitrogen-isotope ratios by adding powdered sugar 1:1 (by mass) and using an 8-s oxygen pulse with a flow rate of 175 mL/min.

It was observed that the elemental copper in the reduction reactor was rapidly exhausted and had to be replaced after approximately 200 samples. As suggested by Gentile et al. [45], analysis of nitrates without the use of an oxygen pulse may increase the lifetime of the reduction reactor. However, this approach would be limited to inorganic nitrogen-containing samples. Our method allows for simultaneous analysis of both inorganic and organic compounds. This is demonstrated with the in-house casein standard (reference value 5.94 ± 0.08‰, measured value 6.04 ± 0.08‰) and the nitrate standard USGS35 (reference value 2.7 ± 0.2‰, measured value 2.62 ± 0.09‰). In addition, analysis of the ammonium nitrate control sample resulted in repeatable \( \delta^{15}N \) values (\( \delta^{15}N_{\text{AIR}} \) -0.41 ± 0.06‰).

### 6.3.2.2 \( \delta^{18}O \) method development

Initial experiments were performed on the 0.6-m long 5-Å molecular-sieve GC column. To evaluate the interference of \( \text{N}_2 \) with \( \delta^{18}O \) measurements, the KNO\(_3\) reference material IAEA-NO-3 was compared to the nitrogen-free benzoic acid reference materials IAEA-601 and IAEA-602. Tailing of the \( \text{N}_2 \) peak into the CO peak was observed for KNO\(_3\) (see Fig. 6.8a), compromising the accurate determination of \( \delta^{18}O \) values as described in section 6.1.2. Even when using maximal dilution with helium to reduce the amount of \( \text{N}_2 \) entering the ion source (Fig. 6.8b) the \( \text{N}_2 \) interference remained a problem. Calibrated to the VSMOW-scale using IAEA-601 and IAEA-602, IAEA-NO-3 showed a \( \delta^{18}O \) value of 15.68 ± 0.15‰ without He dilution and 27.16 ± 0.50‰ with He-dilution (reference value 25.32 ± 0.29‰). To further minimize the \( \text{N}_2 \) interference, the 0.6-m GC column (80–100 mesh) was replaced by a 1.5-m column (60–80 mesh), improving the separation between \( \text{N}_2 \) and CO as shown in Fig. 6.8.

We observed that the combustion of nitrates resulted in CO peaks that were low in intensity and tailing and the CO yields and \( \delta^{18}O \) values from replicates were inconsistent. As described in section 6.1.2, the combustion of nitrates can be improved by the addition
of nickelized carbon (NiC). Fig. 6.9 shows that addition of NiC did not affect the conversion of benzoic acid to CO, but significantly improved the conversion of sodium nitrate (USGS35).

![Chromatograms of N₂ and CO obtained after HTC of KNO₃ using (a) a 0.6-m 5-Å molecular-sieve GC column (80–100 mesh); (b) a 0.6-m GC column combined with He-dilution of the N₂ peak; (c) a 1.5-m GC column (60–80 mesh) and (d) a 1.5-m GC column combined with He-dilution of the N₂ peak. The rectangular peaks at the beginning and at the end of the chromatogram represent CO reference-gas pulses.](image)

**Fig. 6.8.** Chromatograms of N₂ and CO obtained after HTC of KNO₃ using (a) a 0.6-m 5-Å molecular-sieve GC column (80–100 mesh); (b) a 0.6-m GC column combined with He-dilution of the N₂ peak; (c) a 1.5-m GC column (60–80 mesh) and (d) a 1.5-m GC column combined with He-dilution of the N₂ peak. The rectangular peaks at the beginning and at the end of the chromatogram represent CO reference-gas pulses.

Ammonium nitrate samples were analyzed as described in section 6.2.3.2 and calibrated to the international VSMOW-SLAP scale using USGS34 (KNO₃) and USGS35 (NaNO₃) reference materials. The latter are chemically more similar to AN than benzoic acid. IAEA-NO-3 and one of the ammonium nitrate samples were used as control samples.
during each sequence for quality assurance. This resulted in corrected $\delta^{18}O$ values of $25.47 \pm 0.47 \ (n = 38)$ for IAEA-NO-3 and $22.23 \pm 0.72 \ (n = 46)$ for AN$_{QC}$.

Within-sequence repeatability was in the order of 0.1–0.3‰ ($1\sigma$) for both the nitrate standards and the AN samples. The between-sequence variability was found to be larger (0.3–0.8‰), probably due to the hygroscopicity of ammonium nitrate. Despite our extensive drying procedure and despite containing the MAS 200R autosampler in a box flushed with argon, our setup is not completely closed and some water absorption may have occurred. The use of a ‘zero-blank’ autosampler [47] may prevent water absorption and reduce the between-sequence variability.

**Fig. 6.9.** Conversion of IAEA-601, IAEA-602 (benzoic acids) and USGS35 (sodium nitrate) with and without NiC.

**6.3.2.3 IRMS sample analysis**

All AN samples were analyzed for their $\delta^{15}N$ and $\delta^{18}O$ ratios using the methods described before (Fig. 6.10). The $\delta^{15}N$ values for the AN samples ranged between -1.6‰ and +4.8‰ and the $\delta^{18}O$ values between +16.8‰ and +24.8‰. These results fall within the $\delta^{15}N$ and $\delta^{18}O$ ranges for fertilizers as reported by Kendall [9]. The majority of AN samples exhibit $\delta^{18}O$ values between +21‰ and +24‰. Most of these samples originate from Western or South-Western European countries. AN produced in North-Western or North-Eastern European countries (countries 2, 4 and 6) show more depleted $\delta^{18}O$ values. One of the
samples originated from a non-European country (country 3; South America). Although this sample does not exhibit very distinct $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values compared to European samples, it can be differentiated from all other samples. As both the nitrogen and oxygen in ammonium nitrate originate from atmospheric $\text{N}_2$ ($\delta^{15}\text{N} = 0\%$) and $\text{O}_2$ ($\delta^{18}\text{O} = +23\%$) respectively, the observed isotope ratios of ammonium nitrate are scattered around these values [9]. Fractionation can occur during AN production resulting in variation in both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values for different samples. Additives such as dolomite and gypsum also contribute to the isotope signature of the AN samples.

![Graph showing isotope ratios](image)

**Fig. 6.10.** Nitrogen- and oxygen-isotope ratios recorded for all AN samples.

### 6.3.3 Combining elemental and isotope profiles

Although elemental profiles using the 32 detected elements are highly characteristic, samples are still classified together as shown in Fig. 6.3. For example, samples from country 2 are grouped together with AN samples classified as type 2 and type 4 based on their elemental profiles. However, AN originating from country 2 can be completely distinguished from other AN samples based on their isotopic composition (Fig. 6.10). In addition, both type-1 and type-2 AN samples from country 1 exhibit a similar isotopic composition, but these can be distinguished from each other using elemental profiling.
Likelihood ratios can be calculated to determine the strength of matching profiles and the ability to discriminate between samples with different origins. In forensic science, the likelihood-ratio (LR) approach is often used to evaluate the evidential value (see for example Aitken and Taironi [1]):

\[
LR = \frac{P(E|H_p)}{P(E|H_d)}
\]

(6.1)

The probability of finding specific evidence \( (E; \text{combined elemental and isotope profile}) \) is considered given two different hypotheses \( (H_p \text{ and } H_d) \):

\( H_p \): The samples are from the same batch\(^3\)
\( H_d \): The samples are from different batches.

Using the LR approach requires calculation of the distributions of \( E \) that can be obtained under \( H_p \) or \( H_d \). Estimating these two probability distributions is relatively simple if the data is univariate. For example, one can suppose that both distributions are Gaussian and simply estimate the value of the mean and the standard deviation for both. Other methods, like kernel density estimation, can be used to accommodate for more flexible distributions. However, it becomes more difficult when the distributions to be modelled are of multivariate nature. In this case, several approaches are possible. The straightforward solution is to directly calculate the multivariate distribution using the same techniques used in the univariate case (e.g. assume a multivariate Gaussian distribution or use a multivariate kernel density estimates). However, for this approach to function, the sample size should be large enough to calculate the distribution with enough accuracy, rendering the method not useful in practice. Other approaches have been proposed. One simple method is to calculate a similarity metric between pairs of objects, and calculate the distributions for this metric under \( H_p \) and \( H_d \). As the similarity metric is univariate, the problems associated to the accuracy of estimating multivariate distributions are overcome. However, if a similarity metric is used, some information is lost since only the comparison (and not the absolute values) of the measurements are

\(^3\) Here, ‘batch’ can be replaced by either ‘manufacturer’ or ‘type of AN’.
taken into account. Another proposal to overcome the problem of the multivariate nature is to reduce the dimensionality of the data. A common technique is to use principal component analysis (PCA) and retain only a few principal components. This method has been used to analyze datasets containing elemental profiles obtained using ICP–MS for glass [49], soils and sediments [50], and micro debris [51]. Although PCA has the advantage of obtaining an orthogonal basis to describe the data (the covariance matrix has only elements in the diagonal), it shows the disadvantage of having to select a proper number of principal components. This may represent a problem, as the different PCA models (with different numbers of principal components) yield different LR values, and the method shows a lack of robustness. In the present case, we have explored the use of linear discriminant analysis (LDA) [52] instead. Similarly to PCA, LDA finds directions in space to reduce the data dimensionality. However, contrary to PCA, these directions in space are found to establish maximum discrimination between two groups (i.e. ‘same’ or ‘different’). Therefore, LDA is a supervised pattern recognition method. It is not the purpose of this thesis to discuss deeply the advantages of LDA over PCA as a dimension reduction. On a practical level, however, two main advantages can be outlined. First, LDA will define one direction in the multivariate space per number of classes minus one. As the study is restricted always to only two classes (H_p and H_d), only one direction in the space is defined. In other words, only one ‘principal component’ (in this context called ‘canonical variate’) has to be selected. This eliminates the ambiguity of having to select a determined number of principal components, as would happen with PCA. Another advantage is that LDA finds directions in space that are directed to separate the two classes as much as possible, and therefore the discrimination power of the likelihood ratio is optimized. This does not happen when PCA is used, as this is an unsupervised technique. In the end, elemental analysis results in a large number of continuous variables (concentrations of each element), the number of which are reduced to a scalar, so-called canonical variate. Each canonical variate is a linear combination of the original variables. In order to assess the significance of including the isotope ratios, LDA was performed using the levels of 32 elements, as well as on a complete dataset, in which the δ^{15}N and δ^{18}O isotope ratios were included.
Fig. 6.11. Frequency distribution obtained using LDA for ‘same’ and ‘different’ samples at three levels of discrimination using either the complete dataset (32 elements plus two isotope ratios) with (a) manufacturer, (b) type of AN, (c) batch, or the data on the 32 elements only, with (d) manufacturer, (e) type of AN, (f) batch.
We have considered three levels of discrimination, *i.e.* manufacturer, type of AN, and batch. The distributions for ‘same’ and ‘different’ samples were calculated for the complete dataset using LDA (Fig. 6.11a–c). Based on these distributions, samples from the same manufacturer (manufacturer A, country 1), can be discriminated from all other manufacturers. This is also the case for samples from the same type (type-1 AN) compared to all other types (Fig. 6.11b). However, samples from a single batch (the batch of type-1 AN sampled during every hour of production) show slight overlap with samples from other batches. This may be due to the fact that the ‘different’ batches also include type-1 AN samples, which exhibit a similar elemental composition as the ‘same’ samples.

The canonical variates for each variable are shown in Fig. 6.12. Canonical variates are, of course, different depending on the factor used to discriminate (type, manufacturer or batch). Elements or isotopes with canonical-variate values close to zero do not contribute to the discrimination between the two groups of samples. Elements or isotopes with large values (either positive or negative) are important for discrimination. Variables that are highly discriminative on manufacturer level are the elements Mg, Ca and Sr and the $\delta^{15}$N isotope ratio. The elements Li, Mg, Ca, Fe, Co, Ni, Ga, Sr and Ba are important for both the discrimination based on type of AN, as well as on batch level.

![Canonical variates explaining the importance of each variable (element or isotope ratio) in differentiating between AN samples at the three levels of discrimination.](image-url)
Next, the performance of the model (in terms of discrimination power) was assessed. Since LDA constitutes a modeling step, care should be taken to avoid overfitting, which would lead to optimistic assessment of the discrimination power. To this end, the accuracy of the methodology was measured in a 10-fold cross-validation strategy. More specifically, the specificity and sensitivity were calculated for the validation subsets. The specificity represents the true-negative rate, and the sensitivity the true-positive rate. The results (Table 6.3) support the observation from Fig. 6.11 that the most complete separation is obtained when discriminating between the types of AN. The lowest performance, with relatively low true-negative rates, is obtained when classifying samples based on the batch level.

**Table 6.3.** Sensitivity (true-positive rate) and specificity (true-negative rate) for the LDA model to discriminate between ‘same’ and ‘different’ samples at manufacturer, batch, and type level based on the elemental composition only or on the combined elemental and isotope profiles. Results were obtained using a 10-fold cross-validation strategy.

<table>
<thead>
<tr>
<th></th>
<th>Manufacturer</th>
<th>Type</th>
<th>Batch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Elements + isotopes</td>
<td>Elements only</td>
<td>Elements + isotopes</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>0.998</td>
<td>0.998</td>
<td>0.959</td>
</tr>
<tr>
<td>Specificity</td>
<td>0.846</td>
<td>0.817</td>
<td>0.915</td>
</tr>
</tbody>
</table>

As described above, elemental profiles are highly characteristic, but the use of IRMS provides an additional source for discrimination. As observed from Fig. 6.12, both the $\delta^{15}$N and $\delta^{18}$O contribute to discrimination between AN manufacturer, type, and batch. LDA was also performed on the elemental profiles only, resulting in very similar distributions as those shown in Fig. 6.11a–c, although slightly less discrimination power was observed for the manufacturer and batch comparisons (Fig. 6.11d–f). This resulted in a decrease in both sensitivity and specificity for the discrimination on batch level (Table 6.3). When the isotope ratios were excluded for comparing samples on manufacturer level, a lower specificity was obtained (true negatives, 0.846 vs. 0.817 for including and excluding the isotope ratios, respectively). The performance of the LDA model for discriminating between different types of AN was similar when the isotope ratios were excluded. This can be explained by the fact that the type of AN is defined by
the amounts and types of additives used. These additives mainly affect the elemental composition. The performance of the LDA model for LR calculations was evaluated (applying the 10-fold cross-validation again) using Tippett plots [53]. In contrast to the specificity and sensitivity, Tippett plots do not only provide information on the number of misclassifications, but also on the LR values associated with these. Tippett plots show the proportion of cases where the LR values are greater than a given LR (i.e. \( P(\text{LR}(H_i) > \text{LR}) \)) for both the samples that are the same (Hₚ) and that are different (Hₐ). Fig. 6.13 shows that the majority of ‘same’ samples are correctly classified. The LR distributions for samples from the same type and different types of AN (Fig. 6.13b) are well separated and show that extremely high LR values can be obtained. LR distributions for batch-level comparisons (Fig. 6.13c) are less separated and the LR distribution for samples from different batches shows that the number of false positives (‘different’ samples with

![Tippett plots showing the LR distributions calculated with LDA for samples originating from the same or from different manufacturers (a), type of AN (b), or batches (c).](image-url)
LR > 1) is considerable and these can exhibit fairly high LR values. The reason for this is that the relative frequency distributions calculated with 10-fold cross-validation exhibit more overlap than shown in Fig. 6.11c. The frequency distribution for the ‘different’ samples crosses the frequency distribution for the ‘same’ samples on both sides of this curve, resulting in the larger proportion of ‘different’ samples with LR > $10^{10}$ compared to the samples that are from the same batch. These results indicate that comparisons at the batch level are difficult, especially when high LR values are obtained. However, one should be careful in drawing conclusions on the Tippett plots with very low or very high LR values ($<10^{-10}$ or $>10^{10}$), since this involves estimations of LR at the wings of the distribution, which are fairly inaccurate. Therefore, more research will be required to improve the calibration of the LR method [54].

6.4 Conclusion

In the area of forensic explosives analysis chemical profiling can be used to determine whether material recovered from a crime scene and material associated with a suspect are from the same source. This chapter described the combination of elemental and isotope profiling to discriminate between ammonium nitrate (AN)-based fertilizers from different sources. AN is widely available and frequently encountered in improvised explosives. A total of 32 elements were detected in different AN samples obtained from fertilizer manufacturers using ICP–MS, resulting in highly characteristic profiles. The elemental composition of AN samples was found to depend on the type of AN and on the production location. Due to inhomogeneity of the AN granules, the use of laser-ablation ICP–MS was not successful for elemental profiling of single granules. In addition, two methods were developed to determine $\delta^{15}$N and $\delta^{18}$O isotope ratios in ammonium nitrate. Although sample preparation for IRMS is time consuming, IRMS analysis provides an extra source of discrimination in addition to elemental profiling. Likelihood ratios were calculated using linear discriminant analysis (LDA). It was demonstrated that it is possible to discriminate between samples from different manufacturers and between different types of AN. Discrimination between different batches of AN was shown to be more difficult.
References


Isotopic and elemental profiling of ammonium nitrate


