



## Elemental source attribution signatures for calcium ammonium nitrate (CAN) fertilizers used in homemade explosives



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### ABSTRACT

Calcium ammonium nitrate (CAN) is a widely available fertilizer composed of ammonium nitrate (AN) mixed with some form of calcium carbonate such as limestone or dolomite. CAN is also frequently used to make homemade explosives. The potential of using elemental profiling and chemometrics to match both pristine and reprocessed CAN fertilizers to their factories of origin for use in future forensic investigations was examined. Inductively coupled plasma-mass spectrometry (ICP-MS) was used to determine the concentrations of 64 elements in 125 samples from 11 CAN stocks from 6 different CAN factories. Using Fisher ratio and degree-of-class-separation, the elements Na, V, Mn, Cu, Ga, Sr, Ba and U were selected for classification of the CAN samples into 5 factory groups; one group was two factories from the same fertilizer company. Partial least squares discriminant analysis (PLSDA) was used to develop a classification model which was tested on a separate set of samples. The test set included samples that were analyzed at a different time period and samples from factory stocks that were not part of the training set. For pristine CAN samples, i.e., unadulterated prills, 73% of the test samples were matched to their correct factory group with the remaining 27% undetermined using strict classification. The same PLSDA model was used to correctly match all CAN samples that were reprocessed by mixing with powdered sugar. For CAN samples that were reprocessed by mixing with aluminum or by extraction of AN with tap or bottled water, correct classification was observed for one factory group, but source matching was confounded with adulterant interference for two other factories. The elemental signatures of the water-insoluble (calcium carbonate) portions of CAN provided a greater degree of discrimination between factories than the water-soluble portions of CAN. In summary, this work illustrates the strong potential for matching unadulterated CAN fertilizer samples to their manufacturing facility using elemental profiling and chemometrics. The effectiveness of this method for source determination of reprocessed CAN is dependent on how much an adulterant alters the recovered elemental profile of CAN.

### 1. Introduction

Calcium ammonium nitrate (CAN) is a widely available inorganic fertilizer that is frequently used by terrorists and insurgents to make homemade explosives (HMEs) for improvised explosive devices [1,2]. CAN consists of ammonium nitrate (AN), at approximately 75% (w/w), mixed with some form of calcium carbonate such as limestone or dolomite [3–5]. AN is the oxidizing component in many binary HMEs. CAN fertilizer can be reprocessed to make a HME by first mixing it with hot water to separate the soluble AN from the inert and insoluble components (e.g., calcium carbonate), followed by evaporation to

recover pure AN which is dried and crushed [6]. Alternatively, CAN fertilizer can also be crushed to a powder and used directly without extraction of the inert material [6,7]. The final reprocessing step requires mixing the extracted AN or powdered CAN with reducing agents such as aluminum powder, powdered sugar, fuel oil or a combination to produce an explosive mixture [6]. Reprocessed CAN, at one point, was used as the primary explosive in over 85% of the improvised explosive devices used against coalition forces in Afghanistan [1,2]. CAN's wide availability as a legitimate fertilizer will continue to make it and other AN based fertilizers a global HME threat for the foreseeable future. Hence efforts are underway to examine new

*Abbreviations:* CAN, Calcium ammonium nitrate; AN, Ammonium nitrate; HME, Homemade explosives; ICP-MS, Inductively coupled plasma-mass spectrometry; FTIR, Fourier-transform infrared spectroscopy; DCS, Degree-of-class separation; HCA, Hierarchical cluster analysis; PCA, Principal Component Analysis; PLSDA, Partial least squares discriminant analysis; DI, Deionized; RSD, Relative standard deviation

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**Table 1**  
CAN stocks and number of stock samples used in each sample set.

Stock ID	Source	Manufacture date	Set 1 May 2013 <sup>a</sup>	Set 2 Jan 2015 <sup>a</sup>	Set 3 May 2015 <sup>a</sup>
A12	Factory A	2012 (1st Qtr.)	3 (6 <sup>b</sup> )	3	8 (6 <sup>b</sup> )
B98	Factory B	1998	3	3	4 (6 <sup>b</sup> )
B12	Factory B	2012	3	3	4
B13	Factory B	2013	3 (6 <sup>b</sup> )	3	4
C11	Factory C	2011 (17 May)	3	3	4
C12	Factory C	2012 (25 Apr)	–	3	4
C13	Factory C	2013 (22 Mar)	–	3	4
D13	Factory D	2013	–	3	3
E13a	Factory E	2013	–	3	2
E13b	Factory E	2013	–	3	2
F83	Factory F	1983	–	3	8 (6 <sup>b</sup> )

<sup>a</sup> time period CAN samples were prepared and analyzed by ICP-MS.

<sup>b</sup> number of “reprocessed” CAN samples that involved crushing CAN and mixing it with either sugar, aluminum or non-DI water.

analytical approaches for establishing the origin of CAN and other HME precursors to support forensic investigations such as those that aim to identify and disrupt illicit HME-precursor distribution networks.

CAN fertilizers, like AN fertilizers, are available as prills or granules that are typically white, grey or beige in color and 2–5 mm in diameter. CAN fertilizer is produced in various closely related formulations by mixing concentrated AN with finely ground limestone or dolomite resulting in a CAN product that is 20–28% N [8,9]. AN is produced by reacting nitric acid with ammonia. CAN is also made by reacting calcium nitrate with ammonia and carbon dioxide to yield a mixture of AN and calcium carbonate containing 20–26% N [8]. Due to its hygroscopic nature, CAN is coated with anticaking agents and additives such as gypsum, kieselguhr, and magnesium nitrate, which are applied during prilling or granulation [8]. A typical composition of CAN fertilizer consists 27% N (13.5% ammonia-N and 13.5% nitrate-N), 6–9% Ca, and 4% Mg [10], with calcium and magnesium present as carbonates (CaCO<sub>3</sub> and MgCO<sub>3</sub>) as well as oxides (CaO and MgO) [9]. These various constituents and additives could provide unique chemical signatures specific to the manufacturing source of CAN because of bulk and trace compositional differences in CAN that are source dependent. For example, trace elements in the water and mineral additives used in making CAN are dependent on the local geology where acquired and therefore may impart trace elemental signatures into CAN that are source dependent.

There are no previous published works on the source determination of CAN fertilizers. Recent papers have demonstrated the potential of linking AN fertilizers to their places of manufacture using isotopic and elemental profiling [11–13]. In particular, Brust and co-workers used linear discriminant analysis and likelihood ratios to demonstrate the discrimination of AN from one manufacturer from 16 others based on the concentrations of 32 elements and the stable isotopic ratios of oxygen and nitrogen [12]. Their work was quite convincing in part because of their large sample collection that included samples from 17 batches and two fertilizer types from one AN fertilizer manufacturer. Similar work has demonstrated the potential of sourcing commercial cyanides to their places of manufacture using isotopic, elemental and ionic profiles combined with chemometric analysis [14]. The work described here further develops the concept of sourcing commercial chemical products to their places of manufacture through the discovery and exploitation of intrinsic chemical signatures in CAN fertilizers. Specifically, the use of elemental profiling to source CAN fertilizers to a larger number of factories than previously shown for AN and cyanide is demonstrated. This includes investigating the sourcing of CAN that has been adulterated by reprocessing methods used for making HMEs. Lastly, the potential of using chemical attribution signatures from specific chemical constituents to obtain a more precise level of source discrimination is illustrated using the water-insoluble components of CAN.

## 2. Materials and methods

### 2.1. CAN stocks and sample sets

A total of 11 stocks of commercial CAN fertilizer (26 – 27% N) that originated from six factories were used in this study. Each stock was a bulk sample of CAN prills or granules made at a specific factory and time period. From this point forth, the term “prills” refers to either granules or true prills. Each CAN stock and corresponding source information (factory and manufacture date) were obtained either from a manufacturer, distributor, or reputable field representative. The factory sites were confirmed using a list of known CAN factories [8]. F83 was the only stock that was not matched to a specific factory, but based on its region of origin and its distinct prill size and appearance was believed to not be from any of the other factories. The identity of each stock was confirmed as CAN by FTIR analysis using a Gemini analyzer (Thermo Scientific). CAN samples from these 11 stocks were prepared and then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) in three sets. Table 1 lists the 11 CAN stocks with their corresponding source information and number of samples taken from each stock for each sample set.

### 2.2. Sample preparation

CAN samples were prepared according to four methods: (1) CAN prills were dissolved in deionized (DI) water to produce a water-soluble portion and a water-insoluble portion, (2) water-insoluble portions were dissolved in nitric acid to produce a solution, (3) CAN prills were crushed and mixed with either aluminum powder or powdered sugar in water to produce a water-soluble portion and a water-insoluble portion, and (4) CAN prills were crushed, mixed with either tap or bottled water, and the supernatant dried to yield ammonium nitrate (AN). Methods (3) and (4) simulated CAN that is reprocessed as part of HME production. For all methods, the vessels in contact with CAN or its solutions were plastic. Details for each method are described below.

For method (1), a total of 95 pristine CAN samples (those in Table 1 not denoted as “reprocessed”) were prepared by mixing 100 mg of CAN prills (typically 2–3 prills) with 10 mL of DI water (18 MΩ•cm from Nanopure, Thermo Scientific) using a 30 s vortex followed by 15 min sonication. Each sample mixture was then centrifuged for 10 min to separate the insoluble components, primarily some form of calcium carbonate. The water-soluble portion of each CAN sample was stored for ICP-MS analysis.

For method (2), 20 mg of a water-insoluble portion was dissolved completely by mixing with 10 mL of 5% nitric acid (Optima, Fisher Scientific) and stored for ICP-MS analysis. This was done for a subset of Set 1 and Set 3 CAN samples.

For method (3), a subgroup of 12 CAN samples from Set 1 and Set 3

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