



Stable isotopic characterization of ammonium metavanadate (NH_4VO_3)

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ABSTRACT

This paper describes hydrogen ($^2\text{H}/^1\text{H}$), nitrogen ($^{15}\text{N}/^{14}\text{N}$), and oxygen ($^{18}\text{O}/^{16}\text{O}$) isotopic characterization of ammonium metavanadate (NH_4VO_3), a toxic industrial chemical (TIC). We analyzed nineteen high purity compounds obtained from nine suppliers, which show large ranges in trivariate stable isotope compositions, nearly 100-fold greater than analytical uncertainty. Covariation between $\delta^2\text{H}$ and $\delta^{15}\text{N}$ values indicates these ratios can be used to trace ammonia compounds, which are critical for the industrial purification of vanadyl ions and precipitation of ammonium metavanadate crystals. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ plot far from the Meteoric Water Line (MWL), and suggest materials and industrial processing may lead to decoupling of H and O isotopes. We show how stable isotope characterization is a valuable forensic tool that discriminates between NH_4VO_3 samples due to differences in source materials, modes of production, and facility location.

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1. Introduction

Hydrogen, carbon, oxygen, and nitrogen, are essential components of many toxic industrial chemicals (TIC). These light elements have multiple stable isotopes, and observed isotopic variations in earth materials are frequently much greater than the precision with which they can be measured with mass spectrometers. Therefore, it is likely that stable isotopic variation in a given TIC will be a critical forensic tool with which to discriminate source terms. This paper describes results for stable isotope ratios $^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$, and $^{15}\text{N}/^{14}\text{N}$, in ammonium metavanadate (NH_4VO_3), a toxic chemical, and shows how these data can be used as a forensic tool to trace materials.

Isotopic abundances of light elements are variable in nature because they are fractionated during chemical, physical, and biological processes. This fractionation reflects isotope exchange reactions and mass-dependent differences in rates of chemical reactions and physical processes (i.e., diffusion, evaporation). Non-equilibrium chemical reactions preferentially concentrate the lighter and less strongly bound of two isotopes into the product, resulting in fractionation. For nearly six decades, when Urey and Epstein first [1,2] linked ^{16}O – ^{18}O isotope fractionation in calcite

and water to temperature dependence, these light element stable isotopes have been used in geochemical investigations to trace process and provenance of earth materials. The scientific literature describing contributions of stable isotope geochemistry in climatology, oceanography, and hydrology is voluminous. During the past decade, studies in other fields have explored the forensic science application of stable isotope ratio measurements [3–5], and how these ratios can be used to authenticate active pharmaceutical ingredients [6,7], to fingerprint biological agents [8], to geo-locate the source of illicit drugs [9–14] and shipping supplies [15], environmental forensic geochemistry [16], and to authenticate food products, like brands of scotch whiskey and beer from specific distillers [17–20]. These applications demonstrate empirically that stable isotopes are a useful forensic tool to fingerprint or individualize a chemical compound.

We hypothesize that any observed variation in bulk stable isotopic abundance of industrial compounds, like ammonium metavanadate depends on the isotopic composition of raw materials, process reactants, and isotopic fractionation during the manufacturing process. Stable isotope characterization would be a critical forensic tool if it can be shown that the bulk isotopic composition of a TIC integrates raw material, process, and plant location. That is, the bulk stable isotope composition of a TIC would reflect the integrated profile of a production facility, that batch-to-batch variability within a production facility would reflect change in raw material and/or production processing, and that there will be measurable variability in the stable isotope abundance of a given TIC produced at different facilities. We show

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through pair-wise statistical analysis of variance that stable isotope characterization is a credible forensic tool that discriminates among ammonium metavanadate with different product and lot numbers.

2. Materials

Ammonium metavanadate (NH_4VO_3) is a yellow crystalline solid that dissolves readily in water, and is a highly toxic fume, mist, or dust (US DOT Division 6.1 poison). The compound is used principally as a luminescent material in the electronic industry and catalyst in the chemical industry [21]. Principal feed materials for producing the compound include ores and combustion ashes of petroleum fuels, which are composed of unburnt carbon, transition (V, Ni, Fe) and heavy metals. There are several US patents, in addition to patents in Germany and Japan, for industrial processes that produce purified (~90%) and high purity (>95%) ammonium metavanadate crystals from ores and petroleum combustion ash [22–24]. In general, industrial production involves grinding, acid leaching, and oxidation of feed material, ion exchange or solvent extraction to purify dissolved vanadium, solution neutralization, addition of ammonia, and finally precipitation and recovery of ammonium metavanadate crystals. For production of purified vanadium pentoxide, V_2O_5 , the NH_4VO_3 crystals are then thermally decomposed (calcination), which releases NH_3 .

From diverse feed stocks, vanadium is dissolved in acidic, oxidizing solutions producing vanadyl ions (VO^{2+}). Residual solids are removed by decantation. Vanadium remains dissolved as the solution is neutralized with sodium carbonate and made basic (pH 7–8) by addition of ammonia gas, ammonium chloride, or ammonium hydroxide to the solution. After several digestion steps, the acidic vanadyl ions are converted to a basic ammonium metavanadate solution. During these stages, the solution is further purified as impurities that precipitate are washed and filtered. In the final stage, ammonium metavanadate crystallizes from solution and is recovered. Higher purification (>95%) is achieved by adding ammonium hydroxide and raising the pH to 9, which causes other transition metal impurities to precipitate while NH_4VO_3 remains in solution. Some industrial methods use solvent extraction and ion exchange to purify vanadium solutions, however most industries rely on the conversion of vanadyl ions to ammonium metavanadate (aq) and subsequent crystallization for purification.

We measured the stable isotopic composition of nineteen NH_4VO_3 samples that were obtained from nine different suppliers (Table 1). All samples are high purity compounds (>99%) that have distinct product and lot numbers. Complete product descriptions are available on request. The suppliers provided certificates of analysis (COA) and country of origin (CoO) for all but two compounds, which are aged material obtained from LLNL labs and the suppliers no longer maintain product records. Also, we requested additional product history including identification of the production facility, but have not received this information, since it is considered proprietary.

Samples are indexed in Table 1 according to country of origin, and sample numbers are not sequential. Suppliers listed in the next to last column represent the distributor of research analytical chemicals, which is not the same as the production facility, and are indicated by integers to simplify discussion. Based on certificates of origin, two samples are from the United Kingdom (UK), four from Germany (GER), eleven from the United States (USA), and two are undetermined (UNK).

3. Stable isotope methods

3.1. Hydrogen and oxygen isotopes

Hydrogen, D/H or $^2\text{H}/^1\text{H}$, and oxygen, $^{18}\text{O}/^{16}\text{O}$ isotope ratios were measured at the University of California Davis Stable Isotope Facility by thermal conversion elemental analyzer (TC/EA) isotope ratio mass spectrometry (IRMS). The facility uses a Heckatech HT Oxygen Analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK). Samples are combusted in a glassy carbon reactor at 1400 °C to CO and H_2O . Oxygen is analyzed as CO, and D/H is analyzed as H_2 (gas). The following certified reference materials were analyzed with the samples to standardize results: IAEA CH7 Polyethylene ($\delta^2\text{H} = -100.3$ VSMOW), NIST 8568 ($\delta^{18}\text{O}$ VSMOW = -27.93), and NIST 8569 ($\delta^{18}\text{O}$ VSMOW = 57.50). All samples were analyzed a minimum of two times, and the standard deviation of the mean value for replicate is shown as error bars in this report. In general, the expected precision for this method is <0.2‰.

3.2. Nitrogen isotopes

An automated, online method that couples an elemental analyzer with an isotope ratio mass spectrometer (EA-IRMS) is used to analyze TIC samples and precursors for nitrogen isotope composition and elemental abundance. Solid samples are loaded into 3.5 mm × 5 mm tin capsules, and weighed out on a Mettler Toledo XP2U microbalance with a target weight of approximately 80 µg of nitrogen. The tin capsules are sealed and loaded onto a zero-blank Eurovector rotary autosampler. Elemental composition and isotope ratios are determined using a Eurovector EA3024 elemental analyzer coupled to a Micromass (now Elementar) IsoPrime gas inlet isotope ratio mass spectrometer. Samples dropped into the EA are combusted at 1020 °C over chromium oxide in a continuous stream of helium carrier gas. The resulting gases then pass through a reduced copper reactor at 650 °C. Following water removal using a magnesium perchlorate trap, the N_2 analyte gases are separated on a 0.7 m GC PLOT column held at 115 °C. The gases enter the IRMS, where the isotope ratios of $^{15}\text{N}/^{14}\text{N}$ are determined based on the ratio of masses and 30/28. The following certified standard reference materials are analyzed along with the samples to standardize the results: USGS-25, USGS-34, USGS-40, IAEA-N1. All samples were analyzed a minimum of

Table 1
Stable isotopic compositions of NH_4VO_3 samples.

Sample	$\delta^2\text{H}(\text{‰})$	+/-	$\delta^{15}\text{N}(\text{‰})$	+/-	$\delta^{18}\text{O}(\text{‰})$	+/-	Group	Country of origin	Supplier
AM-1	-25.7	1.7	4.37	0.07	3.71	0.15	A	UK	1
AM-15	-31.6	1.9	4.65	0.14	-1.01	0.19	A	GER	5
AM-17	-31.5	0.4	4.30	0.03	-1.01	0.02	A	GER	5
AM-4	-10.3	0.8	12.2	0.02	1.02	0.01	B	UK	1
AM-9	-18.4	0.17	12.7	0.07	0.81	0.10	B	GER	9
AM-16	-21.9	0.9	12.4	0.08	0.70	0.43	B	GER	6
AM-19	-14.0	0.5	12.1	0.31	4.96	0.29	B	USA	9
AM-7	12.7	0.17	35.5	0.03	10.2	0.39	C	UNK	9
AM-18	-25.5	0.8	34.4	0.03	5.27	0.29	C	UNK	8
AM-2	-4.08	0.20	4.37	0.03	3.06	1.02	D	USA	1
AM-3	-8.39	0.13	3.08	0.02	1.90	0.34	D	USA	1
AM-5	-2.09	0.28	3.12	0.15	1.09	0.63	D	USA	3
AM-8	-6.6	1.4	3.41	0.16	2.67	0.05	D	USA	2
AM-13	-5.80	0.45	2.90	0.35	3.27	0.62	D	USA	6
AM-14	-9.6	1.5	1.26	0.01	3.04	0.29	D	USA	6
AM-6	-93.2	1.2	1.81	0.07	-6.80	0.99	E	USA	3
AM-10	-99.4	5.3	1.68	0.24	-6.66	1.67	E	USA	7
AM-11	-17.2	1.4	8.92	0.10	-0.86	1.72	F	USA	4
AM-12	-15.9	2.3	8.94	0.15	0.44	0.34	F	USA	6

$\delta(\text{‰}) = (\text{R}_{\text{Sample}}/\text{R}_{\text{Standard}} - 1)$, where R represents $^2\text{H}/^1\text{H}$, $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$. Analytical precision (+/-) is standard deviation of replicate ($n=2$) analyses.

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