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Charcoal and sodium nitrate, the active ingredients in pesticide gas cartridges, are quantified via carbon analysis and ion chromatography, respectively. Linearity was excellent ($R^2 > 0.995$) over a range consisting of 50−150% of the target concentration for both ingredients. The coefficient of variation for the replicate analyses of gas cartridges over multiple days was <4% for both analytes. Using the results from the analysis of two batches of gas cartridges, theoretical populations were modeled and used to determine practical sampling strategies to support a quality control program for a gas cartridge manufacturing operation. This modeling indicates that the analysis of three cartridges from each of five different lots would produce mean values for both active ingredients that are within 5% of the true mean >99% of the time.

Keywords: *Gas cartridge; rodenticide; predacide; nitrate; charcoal; carbon; sampling*

INTRODUCTION

Gas cartridges are used to manage pest rodent and predator populations on rangeland, forest, and ornamental turf such as golf courses and corporate lawns. Target species include moles, ground squirrels, woodchucks, prairie dogs, coyotes, and marmots. Many gas cartridges consist of a cardboard tube that contains the active ingredients sodium (or potassium) nitrate and charcoal. During use, ignited cartridges burn to produce carbon monoxide. Additional ingredients such as fuller's earth and/or borax may be added to control the rate of burn (*1*, *2*). The U.S. Environmental Protection Agency (EPA) requires that chemical analyses be conducted to confirm that the concentrations of the active ingredients in the manufactured cartridges conform to the Confidential Statement of Formulation (*3*). The U.S. Department of Agriculture (USDA), National Wildlife Research Center (NWRC), Analytical Chemistry Project provides analyses to fulfill this requirement for gas cartridges containing fuller's earth and borax manufactured at the USDA's Pocatello Supply Depot.

Previous methodology separated the water-soluble sodium nitrate from the water-insoluble charcoal by octanol/water partitioning of the gas cartridge contents (*4*). Sodium nitrate was then quantified by ion chromatographic analysis of the aqueous phase. The charcoal was recovered from the octanol by filtration. Recovered charcoal was subsequently dried and quantified by gravimetric analysis. The entire charcoal assay (from preparation of the filter paper through the final weighing) often required 5 days to complete. Historically, quality control (QC) recoveries for sodium nitrate averaged around 100% with coefficients of variation (CV) of ~2%. QC recoveries for charcoal were typically >110% with CVs as high as 25%. It is believed these high CV values were attributed to the inactive gas cartridge ingredients contributing to the gravimetric determination for charcoal.

In an attempt to improve the accuracy, precision, and efficiency, we evaluated ashing and carbon analysis for the quantification of charcoal in gas cartridges. Carbon analysis produced significant improvements in accuracy and precision for charcoal determination. Computer modeling was used to estimate the precision of mean charcoal and sodium nitrate values associated with a variety of sampling strategies.

MATERIALS AND METHODS

Sample Preparation. The outer cardboard cylinder of a gas cartridge was pounded with a rubber mallet to loosen the contents of the gas cartridge. The contents (~165 g) were blended in a standard household type blender on low for ~2 min. An aliquot (~50 g) was removed and transferred to a hand-held coffee mill. The gas cartridge contents were then ground for ~30 s to produce a fine powder.

Charcoal Analysis. The carbon contents of charcoal and gas cartridge contents were determined using ASTM D5373 (*5*). Aliquots of the double-ground (blender/coffee mill) gas cartridge contents (~70 mg) or charcoal (~50 mg) were transferred to a combustion crucible. The crucible contents were combusted to carbon dioxide (CO_2) at 1370 °C using a LECO (St. Joseph, MI) CR-12 carbon analyzer. CO_2 was subsequently detected via infrared detection. Oxygen (10 psi) was used as a carrier gas. Percent carbon was determined via a calibration curve (detector response versus percent carbon) constructed from the analysis of external standards (calcium carbonate, NIST Buffalo River Sediment 2704, synthetic carbon, and sucrose). The percent charcoal in the gas cartridge contents was determined by dividing the carbon content of the gas cartridge contents by the carbon content of the pure charcoal.

Nitrate Analysis. An aliquot (~1.00 g) of the double-ground gas cartridge contents was transferred to a 50 mL nalgene centrifuge tube followed by the addition of 30 mL of deionized (DI) water. The centrifuge tube was capped, shaken by hand for ~30 s, and permitted to stand at room temperature for 15 min. The tube was then centrifuged at 5100*g* for 2 min and the supernatant transferred to a 250 mL volumetric flask. The sample was again extracted and centrifuged, and the supernatants were combined. The volumetric flask contents were diluted to volume with DI water. Using a 10 mL disposable syringe and a 0.45 μm nylon filter, ~8 mL of the extract was filtered into a 10 mL test tube. Using a volumetric pipet, 2.00

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mL of the filtered extract was transferred to a 100 mL volumetric flask. The flask contents were diluted to volume with DI water, capped, and mixed by hand. Aliquots were transferred to 8 × 35 mm autosampler tubes for analysis via ion chromatography.

Ion Chromatography. Nitrate was quantified by ion chromatographic analysis of 20 μL aliquots of the aqueous gas cartridge extract using a Dionex (Sunnyvale, CA) series 4500i ion chromatograph equipped with a Dionex anion micromembrane suppressor. Nitrate was separated on a 4 mm i.d. × 25 cm Dionex AS4A anion separator ion chromatography column (10 μm particle size). A mobile phase of 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ was used at a flow rate of 2 mL/min. The regenerant consisted of 25 mN H_2SO_4 at a flow rate of 2.5–3.0 mL/min. Nitrate was quantified using conductivity detection and a calibration curve (detector response versus nitrate concentration) constructed from the analysis of external standards ranging from 20 to 80 μg of sodium nitrate/mL of water.

Accuracy, Linearity, Ruggedness, and Interferences. To determine the accuracy and linearity of the charcoal analysis, a homogeneous mixture consisting of 73.6% sodium nitrate, 12.5% borax, and 13.9% fuller's earth was prepared by mixing in a blender. This homogeneous mixture was blender mixed with charcoal to prepare 10 g batches containing 10, 15, 28, 45, and 50% charcoal. A single sample of each 10 g batch was analyzed. By using this approach, the ratio of sodium nitrate, borax, and fuller's earth in each sample was identical to the target ratios in the manufactured gas cartridges. Percent charcoal versus percent carbon and percent charcoal observed versus percent charcoal were analyzed by linear regression using MS Excel (*6*). Similarly, for sodium nitrate analysis, a mixture containing charcoal, borax, and fuller's earth at 59.55, 19.15, and 21.30%, respectively, was mixed with sodium nitrate to produce three 10 g batches containing 25, 50, and 75% sodium nitrate. This produced mixtures with ratios of charcoal, borax, and fuller's earth that were identical to the target ratios in the manufactured gas cartridges. Seven aliquots of each mixture were analyzed by ion chromatography and observed versus actual percent nitrate concentrations were analyzed by linear regression. To determine the possibility of interferences due to other ingredients, carbon analyses were also conducted on sodium nitrate, borax, and fuller's earth.

To evaluate method repeatability or method ruggedness, a mixture consisting of target concentrations of sodium nitrate (53%), charcoal (28%), fuller's earth (10%), and borax (9%) was prepared. For sodium nitrate analysis, three aliquots were analyzed on six separate days. For charcoal analysis, three aliquots were analyzed on four separate days. Additionally, seven subsamples from a commercially available gas cartridge were analyzed for sodium nitrate and charcoal on a single day.

Sampling Strategies. According to U.S. EPA product testing guidelines, gas cartridges must be sampled and analyzed from five different production lots (*3*). However, there are no guidelines that specify the number of samples that should be analyzed from each lot. To determine the optimal number of cartridges to sample from each lot, one dozen cartridges were randomly selected from each of two lots of gas cartridges. Each lot consisted of 285 cartridges. The charcoal and sodium nitrate contents of each cartridge were quantified as previously described. The resulting data for both lots were combined and treated as representative of the population to be modeled. The data were then analyzed with a bootstrapping technique (*7*) using Resampling Stats software (Resampling Stats, Inc., Arlington, VA). The nitrate and charcoal percent compositions of the gas cartridges were modeled independently. Lots of 285 cartridges were randomly generated from the percent composition data, and the mean percent charcoal and percent sodium nitrate for 5000 of these modeled lots were calculated. A model was developed to determine appropriate sample size to achieve a reasonable probability of selecting a sufficient number of cartridges from each lot such that the mean estimated charcoal and sodium nitrate concentrations from this sample would fall within 3% of the modeled population mean. The model randomly generated 5000 samples of the data with sample sizes of 15, 20, 25, and 50 cartridges. The means for percent charcoal and percent sodium nitrate were calculated for each of these samples. The number of times the sample mean fell within ±3% of the population means for sodium nitrate and charcoal was subsequently determined. Similar analyses were calculated using a sample criteria of ±5%.

Table 1. Standard Certified Limits

nominal concn of ingredient (N)	certified limits for ingredient	
	upper limit	lower limit
$N \leq 1.0\%$	$N + 10\% N$	$N - 10\% N$
$1\% < N \leq 20\%$	$N + 5\% N$	$N - 5\% N$
$20\% < N \leq 100\%$	$N + 3\% N$	$N - 3\% N$

RESULTS AND DISCUSSION

EPA product property test guidelines require the testing of five separate batches of a manufactured pesticide product (*3*). EPA guidelines for certification limits on pesticide products are listed in Table 1. These guidelines require testing and documentation to prove that the sodium nitrate and charcoal concentrations in the manufactured product do not differ from the nominal concentrations by >±3%. As the manufacturing targets for sodium nitrate and charcoal are 53 and 28%, respectively, this prompted us to develop an analytical method that was capable of providing data to document that the mean charcoal concentration of the gas cartridges is between 25 and 31% and that the mean sodium nitrate concentration falls between 50 and 56%.

An atypical challenge associated with this method is that charcoal, an analyte of interest, is a variable and heterogeneous substance. Carbon analysis of samples from eight different batches of charcoal yielded a range of carbon contents from 70.45 to 75.05%. As the carbon content of the charcoal is used to convert the percent carbon data to percent charcoal, it is imperative that the pure charcoal analyzed be representative of the actual material used to produce the gas cartridges.

To test for potential interferences, all gas cartridge ingredients were initially analyzed for carbon and nitrate. Sodium nitrate was the only component that produced a chromatographic response at the retention time for nitrate. With respect to carbon analyses, borax and nitrate yielded carbon levels below the method limit of detection (0.05% carbon = 3 × instrument response for a blank). Analysis of fuller's earth indicated a carbon content of 0.88%. As fuller's earth constitutes only 10% of the formulation, carbon contribution from fuller's earth would contribute only 0.09% to the total carbon content of the formulation. Given that the CV for the carbon analysis was ~1.5%, we deemed the potential contribution of 0.09% carbon content of the fuller's earth to be insignificant.

Linearity. The target concentrations of the manufactured gas cartridge components are 28% charcoal, 53% sodium nitrate, 9% borax, and 10% fuller's earth. Linearity for quantification of charcoal and sodium nitrate was determined over a range of approximately 50–150% of the target concentrations. The carbon analyzer produced a linear response (detector response versus percent carbon) for the analysis of the external standards ($R^2 > 0.995$). As indicated by Figure 1, there is a highly significant linear relationship between the charcoal content of the gas cartridges and the results of the carbon analysis ($R^2 > 0.995$). Additionally, visual

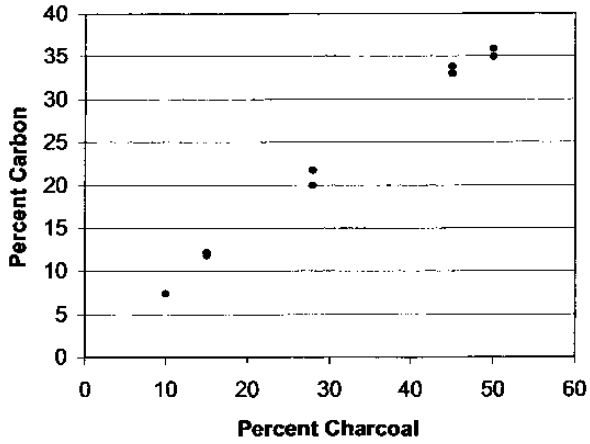

Figure 1. Percent carbon versus percent charcoal from the analysis of gas cartridge mixtures.

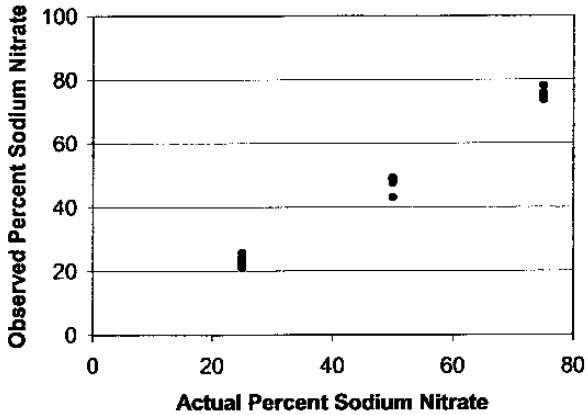

Figure 2. Observed versus actual percent sodium nitrate from the analysis of gas cartridge mixtures.

inspection of the plotted data indicated that the residuals were normally distributed. Additionally, the ratio of carbon/charcoal concentration was nearly constant (CV < 0.05%) throughout the tested range. Linear regression of the log percent charcoal versus log percent carbon plot yielded a slope equal to 1 ($p < 0.001$), suggesting a proportional relationship between these variables. Similarly, the ion chromatography system produced a linear response (detector response versus percent sodium nitrate) for the analysis of the external sodium nitrate standards ($R^2 > 0.995$). The linear regression data presented in Figure 2 shows a highly significant linear relationship between the actual and the calculated sodium nitrate concentrations of the gas cartridge contents ($R^2 > 0.993$). Linear regression of the log observed percent sodium nitrate versus the log actual percent sodium nitrate plot yielded a slope equal to 1 ($p < 0.001$), suggesting a proportional relationship between these variables.

Ruggedness. Twelve replicates of quality control prepared gas cartridge content mixture (containing target concentrations of all ingredients) were analyzed on four separate days. These analyses yielded a mean recovery of 100.7% with a CV of 2.6%. The analysis of seven replicates of a commercially available gas cartridge yielded a CV of only 1.5%. Eighteen replicates of the quality control prepared gas cartridge content mixture were analyzed for sodium nitrate on six separate analysis days. The mean sodium nitrate recovery was 95.3% with a CV of 4.3%. The analysis of seven replicates of a commercially available gas cartridge resulted in a CV of 3.6%. Overall, this approach represents a significant improvement with respect to the gravimetric determination of charcoal content in gas cartridges.

Table 2. Effect of Sample Size on Accuracy

samples per lot	frequency (%) of mean ± 3%		frequency (%) of mean ± 5%	
	charcoal	sodium nitrate	charcoal	sodium nitrate
10	99+	99+	99+	99+
5	96	98	99+	99+
4	93	97	99+	99+
3	90	93	99+	99+
2	82	87	97	98
1	62	72	87	87

Sampling Strategy. To determine the most efficient sampling strategy, 12 gas cartridges were randomly selected from two batches of gas cartridges. Carbon analysis indicated mean charcoal contents of 25.3% (CV = 8.4%) and 26.7% (CV = 5.8%) for the two lots. Ion chromatography analysis indicated mean sodium nitrate concentrations of 59.7% (CV = 5.9%) and 58.8% (CV = 7.1%). These data were used to generate a theoretical population of 5000 lots. Lots of 285 cartridges were then randomly generated from the percent composition data, and the mean charcoal and sodium nitrate contents for 5000 lots were calculated. A model was developed to determine appropriate sample size to achieve a reasonable probability of selecting a sufficient number of cartridges from each lot so that the mean from this sample would fall within 3% of the population mean. The model randomly generated 5000 samples of the data with sample sizes of 15, 20, 25, and 50 cartridges. The mean charcoal and sodium nitrate composition was calculated for each of these samples. As indicated by the data in Table 2, the number of times the sample mean fell within ±3% of the population means for sodium nitrate and charcoal was determined. To obtain a mean value for charcoal and sodium nitrate that falls within 3% of the actual value at least 99% of the time would require the analysis of 10 samples per lot (50 samples total). For our laboratory, this sampling level would be possible to support an initial registration effort. However, as an ongoing quality control program, this level of sampling would be tedious. Table 2 also indicates that when one and two gas cartridges from a lot are sampled, the calculated sample mean for both active ingredients falls within ±5% of the true mean <99% of the time. As we prefer a higher level of precision, we adopted a sampling scheme of three cartridges per lot (15 total), analyzing one subsample from each cartridge. This approach should generate mean values for charcoal and sodium nitrate that are within 5% of the true value >99% of the time. With respect to manufacturing gas cartridges, this level of precision and accuracy should be suitable for the production of a consistently performing product.

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