

Student Skill Development with the Real World: Analyzing *tert*-Butyl Alcohol Content in Gasoline Samples

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ABSTRACT

In the activity described in this communication, the authors present a simple experiment that can be implemented with moderate operational costs and that allows students to acquire the manipulative skills necessary for chromatographic analysis of a familiar fuel that still plays a fundamental role in providing energy for transport of passengers and goods.

The use of gasoline formulations in a laboratory activity presents students with a motivating subject of study and an opportunity to apply analytical procedures to the characterization of controlled substances used in vehicle fuel formulations.

KEYWORDS

Upper-Division Undergraduate, Laboratory Instruction, Analytical Chemistry, Oxygenates, Gasoline, Chromatographic Techniques, Qualitative and Quantitative Analysis

INTRODUCTION

The analysis of gasoline has been the objective of several student experiments over the last two decades¹⁻¹², motivated by the increase in student interest that the use of everyday commodities contributes to practical activities. Experiments with fuels have quantified lead compounds in commercial formulations²⁻⁵ and characterized specific components or additives introduced to substitute organometallic compounds.⁸⁻¹⁰ Previous strategies have applied volumetric and spectroscopic methods^{2-4, 12}, however the most appropriate method for complex formulations is gas chromatography with suitable detectors.^{8,9}

Gasoline chemistry has supported the mechanical development of spark-initiated internal combustion engines (SIICEs) for over a hundred years and significant investment has been rewarded with lucrative commercial returns.¹³

Early fuel formulations were modified to avoid mechanical failure of engine components through “knocking” or “pinking” a process resulting from the ignition of pockets of compressed fuel before the spark-initiated combustion front reached the air-fuel charge. The increase of compression ratios and octane rating to improve power output and energy efficiency of SIICEs required further alterations to fuel formulations. In the 1970s, the introduction of catalytic converters resulted in significant reduction in emissions of CO, hydrocarbon and nitrous oxide in exhaust gases. This improvement was made possible by the substitution of tetramethyl (TML) and tetraethyl lead (TEL) by oxygenated additives that contributed anti-knock and octane boosting properties but did not poison heavy-metal-sensitive catalysts. This new formulation increased performance, improved running economy and reduced volatile organic compound emission.

Fuel additives developed during the last few decades include a range of substances that provide chemical stabilization, oxidation protection, octane enhancement, exhaust gas reduction, detergent action and coloration.¹³ These additives are compatible with the principal component in fuel lines and storage containers throughout the commercial distribution network. The principal “gasoline fraction” is often a mixture of about 200 hydrocarbons with carbon numbers from 4 to 12 and a boiling range between 35 and 200 °C. Octane boosters, as high percentage components, must blend well with the gasoline fraction and reduce carbon monoxide and unburned hydrocarbons in exhaust gas emission. In general, ethers are favored as they perform well under normal engine operating conditions¹³ however, these compounds share the toxicity and environmental consequences of some alcohols, also used as oxygenates.¹⁴⁻¹⁶ Oxygenate addition is permitted up to about 5-6 vol % in USA¹⁷ and 15 vol % in Europe.^{18, 19} In the past, methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), diisopropyl ether (DIPE) tert-butyl alcohol have all been chosen as oxygenates as they perform well under a wide range of engine operating conditions. However, the detection of MTBE and tert-butyl alcohol (TBA) in groundwater close to gasoline spillage sites, led to a major change in fuel formulation policy. Under spill-site conditions, MTBE can be biodegraded into TBA. TBA is toxic, difficult to eliminate due to its water-miscibility and suffers slow

biodegradation. TBA is used in synthesis of MTBE and other ether oxygenates and may be present as a contaminant. Under the Clean Air Act (USA, 2012) producers of fuel and additives are required to provide information regarding the emissions from their products and effects on public health. Largely as a response to these controls most fuel oxygenates in the USA are now based on ethanol.²⁰

Both TBA and MTBE have been detected in seawater, ground and surface water²¹ and in soils. Although the impact of these compounds on human health is not yet clear, strict limits have been imposed on their use in gasoline, and it is therefore essential to evaluate their concentration with accuracy. Evaluation of oxygenate content has been reported by GC^{8,22}, GC-MS⁹, ¹H NMR²³ and FTIR.^{12,24} Gas chromatography is a widely-used quantitative and qualitative instrumental technique introduced in analytical chemistry courses and therefore an essential component of practical classes. In this experiment, students evaluate TBA content of commercial fuels and compare their results with current legislation.¹⁸ The study of real-world samples provides an important stimulus to student interest. This activity has been designed for mid-course students that have completed introductory courses on Organic, Inorganic and Physical Chemistry and are either attending lecture courses on analytical instrumentation or separation techniques. The content is intended to provide a practical experience to support these modules.

EXPERIMENTAL SECTION

Materials and instrumentation

Samples of different brands of gasoline from three suppliers (designated as A, B and C in Table 1) were collected in completely filled and sealed flasks. Samples were cooled, transported to the laboratory and analyzed, without pre-treatment, within 24 h. *Tert*-butyl alcohol with 99.5 % purity was obtained from Acros.

Table 1. Gasoline samples analyzed

Brands	
A	Unleaded 95 Unleaded 98 Unleaded 98 Premium
B	Unleaded 95

Analysis was performed using a CHROMPACK CP 9001 equipped with injector and flame ionization detector temperatures of 190 °C. Samples were characterized in duplicate by injecting 1 μ L samples onto a packed column (2 m x 3.2 mm x 2.1 mm I.D., 10 % Carbowax 20 M with 80/100). The column temperature was maintained at 50 °C for the first three minutes, then increased from 50 to 190 °C at 10 °C/min, and held at this end-temperature for 3 minutes. Data was acquired and stored using DataApex Clarity software installed on a desktop computer.

Preparation of calibration samples

The standard addition method was chosen because of the small amounts of compound present and because of lower detection limit of this method relative to other quantification methods. Six 1 mL solutions were prepared from each gasoline sample and spiked with different volumes of TBA (0, 10, 20, 30, 40 and 50 μ L). It is advisable to prepare each solution immediately before the injection and to use sealed vials with septa to reduce evaporation of volatile components.

Hazards

TBA and gasoline samples are volatile, flammable liquids. Preparation and manipulation should be carried out within a fume hood while using lab coats, gloves and safety spectacles. All chemicals should be disposed of using an appropriate waste container.

RESULTS

To identify the TBA peak in gasoline, prior to quantification, students prepared a standard solution with a small amount of pure TBA compound in acetone. This solution was analyzed using optimized instrumental conditions and the t_r of TBA was determined ($t_r = 6.18$ min). The commercial gasoline samples were characterized using the same experimental conditions and the TBA peak, shown in Figure 1, was identified from its t_r .

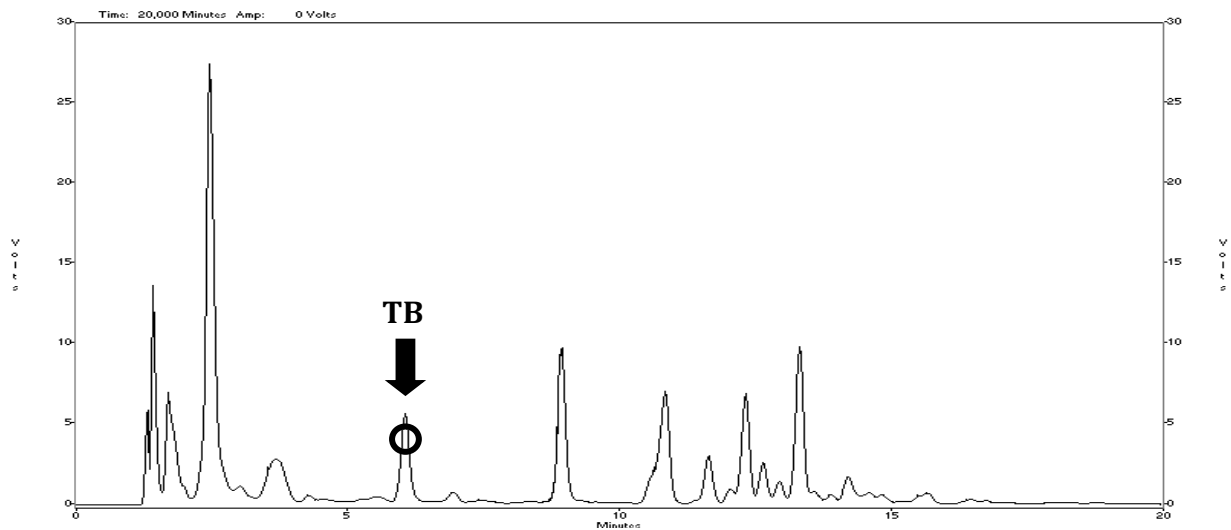


Figure 1. Chromatogram of TBA in gasoline 95 from brand A

Quantitative measurement of TBA using the standard addition method

A known amount of TBA was added to each gasoline sample in accordance with the standard addition procedure. The evaluation of areas under the TBA peaks (Figure 1) and baseline correction was carried out using the same software routines for all samples. TBA peak area (A_{TBA}) was plotted as a function of TBA spike concentration ($C_{TBA \text{ added}}$) in the samples (Figure 2). A linear relationship was observed, according to equation 1, with slope m and intercept b :

$$A_{TBA} = m C_{TBA \text{ added}} + b \quad (\text{equation 1})$$

The original concentration of TBA in the gasoline samples ($C_{TBA \text{ sample}}$) was calculated by extrapolation of the standard addition graph (Figure 2) to $y = 0$ using equation 2:

$$C_{TBA \text{ sample}} = b / m \quad (\text{equation 2})$$

The concentration of TBA was calculated from the slope and intercept of the plots shown in Figure 2.

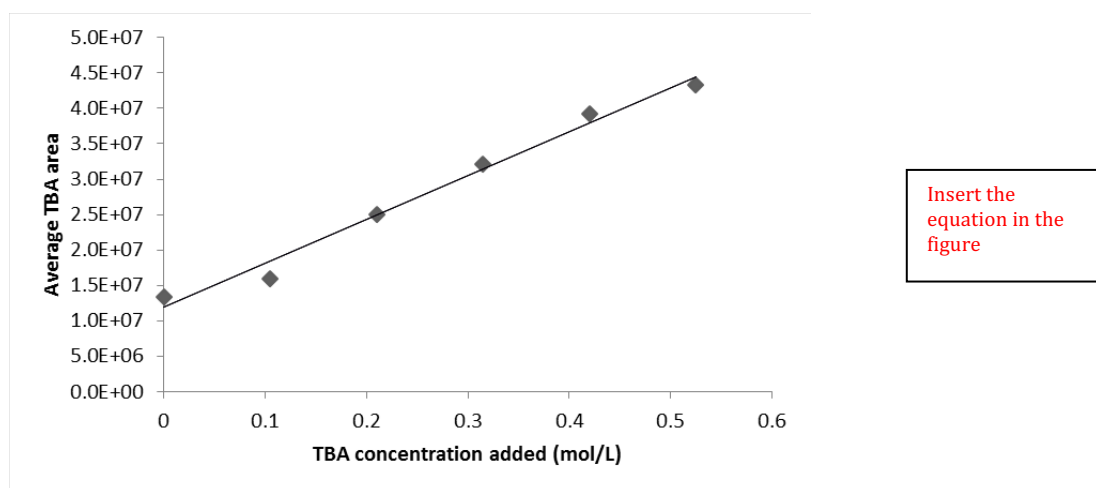


Figure 2. Standard addition plot of TBA in 98 Premium gasoline, brand A

The conversion of concentration of TBA from (mol/L) to % (v/v) was performed according to equation 3:

$$\% [TBA] = \frac{n \cdot M}{\rho \cdot 10^3} \times 100 \quad (\text{equation 3})$$

where n (mol) are the moles of TBA obtained by extrapolation, M (g/mol) is the molecular weight of TBA, ρ (g/cm³) is the density of TBA and 10³ (cm³) is the conversion factor. The quantification and statistical results obtained from the data plotted according to equation 1 are displayed in Table 2 (Supporting information).

Table 2. Quantification of TBA in gasoline samples

Straight line equation	r ^a	DL ^b (mol/dm ³)	QL ^c (mol/dm ³)	x _E ^e ± S _{xE} x t ^e (mol/dm ³)	% ± Δ%
y = [(55 ± 4) x + (16 ± 3)] x 10 ⁶	0.995	0.08	0.26	0.30 ± 0.17	2.8 ± 0.4
y = [(41 ± 4) x + (17 ± 2)] x 10 ⁶	0.996	0.08	0.26	0.40 ± 0.70	3.9 ± 0.5
y = [(62 ± 4) x + (12 ± 3)] x 10 ⁶	0.992	0.08	0.28	0.20 ± 0.10	1.8 ± 0.3
y = [(112 ± 8) x + (20 ± 5)] x 10 ⁶	0.995	0.08	0.26	0.17 ± 0.14	1.7 ± 0.3
y = [(46 ± 5) x + (17 ± 4)] x 10 ⁶	0.991	0.11	0.37	0.37 ± 0.32	3.5 ± 0.7
y = [(60 ± 2) x + (22 ± 2)] x 10 ⁶	0.998	0.05	0.16	0.37 ± 0.11	3.5 ± 0.3
y = [(46 ± 1) x + (17 ± 0.8)] x 10 ⁶	0.9995	0.03	0.10	0.36 ± 0.07	3.5 ± 0.2

^acorrelation coefficient; ^bDL-Detection limit; ^cQL-Quantification limit; ^d|x_E|-TBA concentration; ^eS_{xE} x t- TBA concentration error.

DISCUSSION

Optimization of the temperature program was carried out in preliminary experiments to establish the most favorable conditions used for component separation and characterization. Each sample was chromatographed only twice and the data obtained from the chromatograms were recorded in a table. Students identified TBA in samples using t_r of the compound.

From examination of the standard addition plot obtained from the TBA peak area (A_{TBA}) as a function of concentration of the TBA spike ($C_{TBA \text{ added}}$) (Figure 2), students confirmed the reproducibility of results. In all cases a good correlation coefficient (r) and similar detection (DL) and quantification limits (QL)²⁵ were obtained. The TBA concentration (X_E) was estimated by extrapolation of the standard addition plot to $y = 0$ where the t -student used was 2.776 for 97.5 % probability and 4 ($n-2$) degrees of freedom. The error in volume introduced with the addition of the 50 μL spike was considered to be insignificant and was not taken into account in calculations.^{26, 27}

The value of Student's t used was for 95% probability and $n-2$ degrees of freedom.²⁸

The average value for the concentration of TBA in gasoline obtained by the students was 0.25 mol/L with data ranging from 0.17 to 0.40 mol/L (Table 2). The percentages of TBA obtained after conversion of the concentration of TBA from (mol/L) to % (v/v) were all well below the legal limit of 15 % (v/v).^{18,19}

Students readily arrived at the conclusion that all of the gasoline samples contained TBA within the legal limit established by current legislation.

CONCLUSION

In this communication, the authors describe an experiment prepared for upper-division undergraduates. Student interest is sustained by real-world relevance of the content, with learning objectives that are appropriate for analytical/instrumental laboratory or Environmental Chemistry modules, and hands-on experience in the application of an important chromatographic technique. During this experiment students gain first-hand experience in the application of the standard addition method to analysis with GC equipment

and practice in the interpretation of chromatograms. The experiment is simple, convenient and provides accurate determination of TBA in gasoline. Instructors may use this experiment to encourage their students to consider the errors introduced by the volumetric dilution that occurs as a result of spike addition and the consequences on the analytical data. In many practical classes, due to unavoidable constraints on the duration of laboratory activities, student experiments are limited to a small number of replicas. This limitation naturally has consequences on the precision of the experimental data. Students should be aware that in “real-world” situations these restrictions can be removed.

The relationship between Chemistry and the Environment is almost always complicated by the many physical and chemical interactions involved. This experiment provides an opportunity to study the evolution of a familiar commercial product and how environmental impact has been minimized and the operational benefits maximized. For many students, this leads to a new appreciation of the rather tortuous evolutionary path that chemists must follow to attain the goal of environmentally-conscious production. (1 865 words)

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