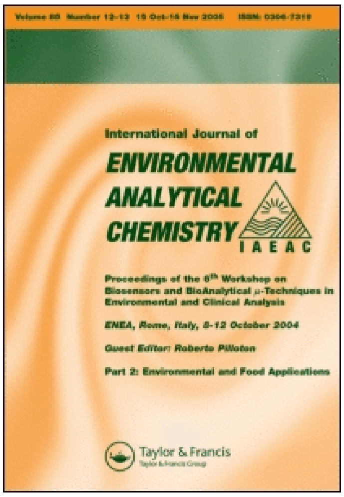
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Microdetermination of Gasoline in Potable Waters by Gas Chromatography?

R. Dell'acqua[a]; B. Bush[a]
[a] New York State Department of Health, Division of Laboratories and Research, Albany, New York, USA

To cite this Article Dell'acqua, R. and Bush, B.(1973) 'Microdetermination of Gasoline in Potable Waters by Gas Chromatography?', International Journal of Environmental Analytical Chemistry, 3: 2, 141 — 146
To link to this Article: DOI: 10.1080/03067317308071075
URL: http://dx.doi.org/10.1080/03067317308071075

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem., 1973, Vol. 3, pp. 141-146
© Gordon and Breach Science Publishers Ltd.
Printed in Great Britain

Microdetermination of Gasoline in Potable Waters by Gas Chromatography[†]

R. DELL'ACQUA and B. BUSH

Division of Laboratories and Research, New York State Department of Health, Albany, New York 12201, U.S.A.

(*Received January 25, 1973*)

KEY WORDS: Hydrocarbons, Gasoline, Gas chromatography, Paraffins, Petroleum.

Downloaded At: 10:01 19 January 2011

Gasoline is extracted with 10 ml of hexane from 2 l of potable water. The hexane solution is analyzed on an SE30 column with flame ionization detection. Gasoline can be differentiated from other petroleum cuts and quantitated to a level of 0.25 mcl/l with a relative standard deviation of ±10%.

INTRODUCTION

Over the past few years there has been an increasing demand for qualitative and quantitative analysis of traces of gasoline in ground water used for drinking. Contamination occurs primarily by leakage of underground storage tanks, runoff from automobile garage facilities, and railroad tanker spillage. Less common, but on a larger scale, is contamination from refineries. Passage through ground water over considerable distances has occurred, even to the extent of causing vapor accumulation in basements with subsequent explosions.

Gasoline contamination is noticeable by the characteristic odor, and at lower concentrations (of the order of 0.25 mcl/l) it is still detectable by taste.[1] At these levels it can be considered miscible with water, either by true dissolution or by sorption by organic material normally present in the water.

[†] Presented at the Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Halifax, N.S., August 23–25, 1972.

Careful analytical procedures are therefore required for the separation and accurate measurement of gasoline in samples of potable water.

Several approaches to this analysis have been made. Fluorescence, utilizing for assay the u.v.-stimulated emission of aromatic constituents,[2] and infrared analysis[3] have been proposed. Neither method is completely satisfactory—the former because of variation in response according to the aromatic content, which may not be known to the analyst; the latter because of the inherently low extinction coefficients of infrared absorptions, a problem which can be overcome only by using the expensive Fourier Transform techniques.

Gas chromatography, on the other hand, allows the mixture of hydrocarbons to be separated roughly into carbon-number groups and isomers, and the response of the flame ionization (FI) detector is relatively high (10^{-10}g). Identification of hydrocarbon spills has been carried out by using both capillary columns[2] and support-coated open tube (SCOT) columns,[4] as well as by metal analysis.[5,6]

In potable water analysis, several liters of water must be extracted with hexane to obtain a signal from the FI detector. The hexane cannot, of course, be evaporated, so a large volume of hexane extract must be injected on to the column. This precludes the use not only of capillary and SCOT columns but also of some designs of FI detector and chromatograph.

The present method has been developed to give highly sensitive quantification of gasoline after extraction from a 2-l sample of potable water and, in the same process, to give rapid identification of other petroleum cuts.

METHOD

Reagents

Hexane used was "Nanograde"; sodium sulfate was analytical-reagent grade, anhydrous, granular.

Gas chromatographic equipment and conditions

Type: Model MT220, manufactured by Tracor, Inc., Austin, Texas.
Column: Glass, U shape, 6 feet long, 1/4 in. o.d., filled with Gas Chrom Q, 80–100 mesh, coated with 4% silicone SE30.
Carrier: Nitrogen (High Purity) at 40 lb pressure; 110 ml/min.
Air: (High Purity) at 40 lb pressure; 285 ml/min.
H_2: (High Purity) at 40 lb pressure; 37 ml/min.

Operating temperatures: Column, programmed from 35° to 175°C at a rate of increase of 7.5°C/min. Injection port, 200°C. Transfer, 200°C. Detector, 275°C.

Downloaded At: 10:01 19 January 2011

Recorder: Operating at 1 mV, full scale, with a chart speed of 30 in./hr. Electrometer sensitivity equal to a background current of 5×10^{-10} amps.

Extraction

As close as possible to the time of analysis (certainly within the preceding 24 hr), 2 l of sample at room temperature are collected in a tightly closed, all-glass container and poured into a 3-l separatory funnel with a Teflon stopcock. Four ml of 50% H_2SO_4 are added, and the contents are mixed. The sample is then extracted with hexane (10 ml) by shaking for 5 min, during which the pressure is released two or three times. After resting for 5 min, the aqueous phase is discharged, and the solvent is collected in a 50-ml beaker. Approximately 0.5 g of anhydrous granular sodium sulfate, wetted with hexane, is added to the beaker and swirled to ensure complete drying, after which the extract is poured into a graduated centrifuge tube. The solvent is brought to volume by adding portions of hexane passed through the tip of the separatory funnel and the beaker.

Gas chromatography

With the oven temperature at 35°C, a portion of the extract is injected on to the column. (To obtain results from a sample with a low contamination, up to 30 mcl may be injected.) When the hexane solvent has practically ceased to be eluted and the pen has reached approx. 75% of full-scale deflection, temperature programming is started.

Downloaded At: 10:01 19 January 2011

RESULTS AND DISCUSSION

Identification

Gasoline is eluted within the first 6 to 8 min after the start of the programmed temperature cycle (Figure 1). Kerosine is eluted between 4 and 16 min after the start of the cycle. Lubricating oils are eluted from 10–15 min up to 25–40 min. (Gas chromatographic analysis of the heavier petroleum cuts will be the subject of a separate paper.)

Quantification

The peak marked with an asterisk in Figure 1 ($6.0\,l \times 10^{-9}$ gasoline, 30-mcl injection) is used as a reference. It belongs to the nonane group and is characteristic of all gasolines, being present in the proportion shown, to a

Downloaded At: 10:01 19 January 2011

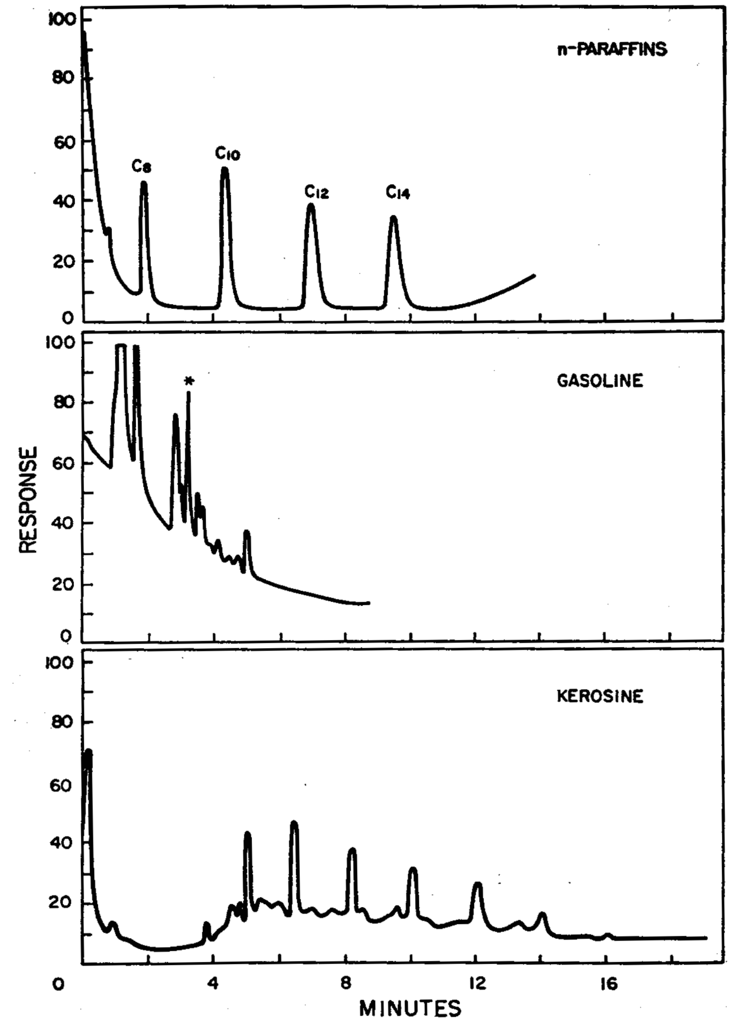


FIGURE 1 Chromatograms from samples of *n*-paraffins, gasoline and kerosine.

first approximation, irrespective of octane rating and source of the product. It is also conveniently at the center of the range of volatility of the cut, so that differential loss of volatiles and consequent changes in proportion of the components will affect quantitation minimally. Observation of the chromatograms of several hundred samples of gasoline extracted from water over the past three years has, however, shown that the general composition of the gasoline does not vary widely from sample to sample, so the error introduced by the differences in volatility of the components is small.

Recorder: Operating at 1 mV, full scale, with a chart speed of 30 in./hr. Electrometer sensitivity equal to a background current of 5×10^{-10} amps.

Extraction

As close as possible to the time of analysis (certainly within the preceding 24 hr), 2 l of sample at room temperature are collected in a tightly closed, all-glass container and poured into a 3-l separatory funnel with a Teflon stopcock. Four ml of 50% H_2SO_4 are added, and the contents are mixed. The sample is then extracted with hexane (10 ml) by shaking for 5 min, during which the pressure is released two or three times. After resting for 5 min, the aqueous phase is discharged, and the solvent is collected in a 50-ml beaker. Approximately 0.5 g of anhydrous granular sodium sulfate, wetted with hexane, is added to the beaker and swirled to ensure complete drying, after which the extract is poured into a graduated centrifuge tube. The solvent is brought to volume by adding portions of hexane passed through the tip of the separatory funnel and the beaker.

Gas chromatography

With the oven temperature at 35°C, a portion of the extract is injected on to the column. (To obtain results from a sample with a low contamination, up to 30 mcl may be injected.) When the hexane solvent has practically

effect could not be exploited because a solvent with a high affinity for gasoline was required to scavenge the gasoline from the water; pentane is too volatile for precise handling in the laboratory. The combination of injector temperature, temperature program, detector, and column design described above was the only successful combination of many tried. Resort to a "heart cutting" technique[7] might make a different method feasible, but the present method does not require such elaboration.

CONCLUSION

Gasoline can be differentiated from other petroleum cuts by gas chromatography and quantitated at a level of 0.25 mcl/l with a rel. S.D. of ±10%.

References

1. R. Dell'Acqua, *Chromatographic Analysis of the Environment* (Marcel Dekker, N.Y., in press).
2. P. R. Mackie, A. S. McGill, and R. Hardy, *Environ. Pollut.* 3, 9 (1972).
3. J. S. Mattson, H. B. Mark, R. L. Kolpack, and C. E. Schutt, *Anal. Chem.* 42, 234 (1969).

Downloaded At: 10:01 19 January 2011

4. I. Halász and C. Horváth, *Anal. Chem.* **35,** 499 (1963).
5. J. V. Brunnock, D. F. Duckworth, and G. G. Stephens, *J. Inst. Petr.* **54,** 310 (1968).
6. H. R. Lukens, D. Bryan, W. A. Hiatt, and H. L. Schlesinger, *Rep. Atom. Energy Comm. U.S. GULF-RT-A-10684.*
7. D. R. Deans, *Chromatographia* **1/2,** 18 (1968).

Downloaded At: 10:01 19 January 2011