Consumer Product Propellant Analysis and an Alternative Standard Blending Technique for High Concentration Standards

Application Note

Environmental

Authors

Wendy Howard
California Air Resources Board
PO Box 2815
Sacramento, CA 95812
USA

Shannon Coleman
Agilent Technologies, Inc.
5301 Stevens Creek Blvd
Santa Clara CA 95051
USA

Abstract

An Agilent Technologies gas chromatograph (GC) configured with an automated 6-port gas sample valve, a split injection inlet, an HP-PLOT Q capillary column and a thermal conductivity detector for the analysis of common aerosol propellants: carbon dioxide (CO_2), propane (C_3,H_8), isobutane (C_4H_{10}), n-butane(C_4H_{10}), 1,1-difluroethane (HFC-152a), 1,1,1,2-tetrafluroethane (HFC-134a), and dimethyl ether (C_2H_6O). Six methods are configured with six different split ratios to allow for a six point calibration curve for each standard. A method is provided to dynamically dilute samples when a multipoint calibration is desired across a narrow calibration range from a single standard.

Agilent Technologies

Introduction

A variety of consumer and industrial products are packaged in self pressurized or aerosol containers. The aerosol propellant usually consist of a mixture of volatile organic compounds (VOCs), which can result in ground level ozone, a smog component that is detrimental to human health. Products using these propellants can range from spray paints, hairsprays, cleaning and household products to industrial sealants and lubricants. About nine billion aerosol units were produced worldwide in 1998. The vast majority of these products were produced by the United States (three billion) and Europe (four billion). In the early 1990s, the United States began to develop a regulation to limit the VOC content in consumer products. The U.S. Environmental Protection Agency has now imposed minimum national standards for VOC emissions.[1]

In this study, we look at a gas chromatography method for the analysis of some common aerosol propellants: carbon dioxide (CO_2), propane (C_3,H_8), isobutane (C_4H_{10}), n-butane(C_4H_{10}), 1,1-difluroethane (HFC-152a), 1,1,1,2-tetrafluroethane (HFC-134a), and dimethyl ether (C_2H_6O). We also demonstrate a method of performing a six point calibration by using the split inlet as a dynamic diluter.

Experimental

Standards and reagents

The standards and reagents used are listed in Table 1.

Table 1. Standards and Reagents

Standard	Reagent		
1	HFC-134a, HFC-152a, and CO_2	Matheson- Trigas	33% Each
2	Butane, propane, isobutane, Dimethyl ether	Matheson-Trigas	25% Each

Instrument

The analysis was performed on an Agilent 7890A gas chromatograph equipped with a 6-port gas sample valve, a split/splitless capillary inlet, an HP-PLOT Q capillary column and an Agilent thermal conductivity detector.

Sample preparation

All samples were prepared by loading Tedlar sample bags from a bulk supply standard. All standard concentrations are stated in percent volume. Calibration samples were prepared from the stock gas cylinders provided by Matheson-Trigas. Stock standard solutions used in calibrations are described as Standard 1: HFC-134a (33%), HFC-152a (33%), and carbon dioxide (33%); and Standard 2: propane (25%), n-butane (25%), isobutane (25%), and dimethyl ether (25%). Standards are diluted across six points using varying split ratios for each method.

Analysis parameters

The GC parameters used in the analysis of propellant are shown in Table 2.

Table 2. Gas Chromatograph

GC run conditions			
Analytical column	HP-PLOT Q, 30 m × 0.53 mm × 40 µm		
Gas sample loop vol	0.1 mL		
Inlet temperature	200 °C		
Inlet pressure	6.1513 psi		
Carrier gas	Helium, constant flow mode, 7.0 mL/min		
Split ratio/flow	Method (%)	Split ratio	Split flow (mL/min)
	5	47.114:1	329.8
	10	22.843:1	159.9
	20	10.707:1	74.949
	50	3.425:1	23.975
	75	1.8:1	12.6
	100	1:1	7
Oven program	100 °C (4.0 min hold), 10 °C/min to 160 °C (2.0 min hold)		
Column velocity	54.189 cm/s		
Injection	Non-heated gas sample valve		
Transfer line temperature	Ambient		
Detector	TCD		
Detector temp	160 °C		
Reference flow	15 mL/min		

Results

The HP-PLOT Q column provides baseline resolution for the seven propellants analyzed. The inlet split ratio was varied to obtain a calibration curve across six points. See Tables 3 and 4 for a correlation of split ratio to percent volume of component injected. Linearity was good for all seven components with R^2 ranging from 0.9982 to 0.9994. Figures 3 and 4 show the calibration curves for each component by varying the inlet split ratio from 1:1 to 47:1.

Figure 1 Shows good resolution and sensitivity between carbon dioxide, HFC-134a, and HFC-152a at a concentration of 33% volume each on a TCD using the method parameters for screening.

Figure 2 shows good resolution and sensitivity between propane, dimethyl ether, isobutane, and n-butane at a concentration of 25% volume each on a TCD using the method parameters for screen screening.

Table 3. Table of TCD Response

Amount (% vol)	Split ratio	Carbon dioxide	HFC-134a	HFC-152a
1.65	47.114:1	1087.4	1660	1381.2
3.30	22.843:1	2051.7	3077.5	2772.1
6.60	10.707:1	4135.1	6472.5	5750.1
16.50	3.425:1	10162.3	16429.2	14298.9
24.75	1.8:1	14832.8	24254.5	20917.5
33.00	1:1	19122.8	31600.1	27201.5

Table 4. Table of TCD Response

Amount (% Vol)	Split ratio	Propane	Dimethyl ether	Isobutane	n-Butane
1.25	47.114 : 1	1334.7	1231	1561.5	1619
2.50	22.843 : 1	2960.3	2660.6	3513.8	3628
5.00	10.707 : 1	6113.8	5533.3	7280.5	7549
12.50	3.425 : 1	14875.5	13527.8	17859.6	18629.3
18.75	1.8 : 1	21761.5	19797.5	26245.2	26724.3
25.00	1 : 1	28315.7	25563.2	34117.2	34734.5

Table 5. Linear Regression Analysis

Compound	R^2
Carbon dioxide	0.9984
HFC-134a	0.9994
HFC-152a	0.9991
Propane	0.9989
Dimethyl ether	0.9986
Isobutane	0.9991
n-Butane	0.9982

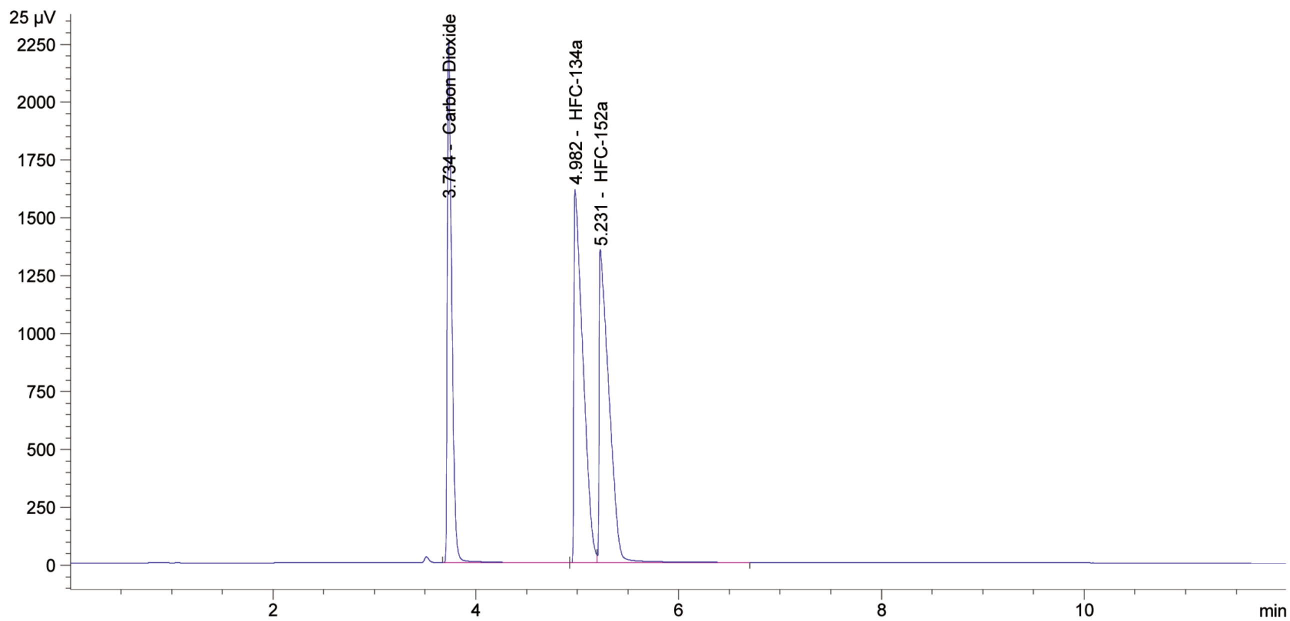

Figure 1. Chromagram of CO_2, HFC-134a, and HFC-152a.

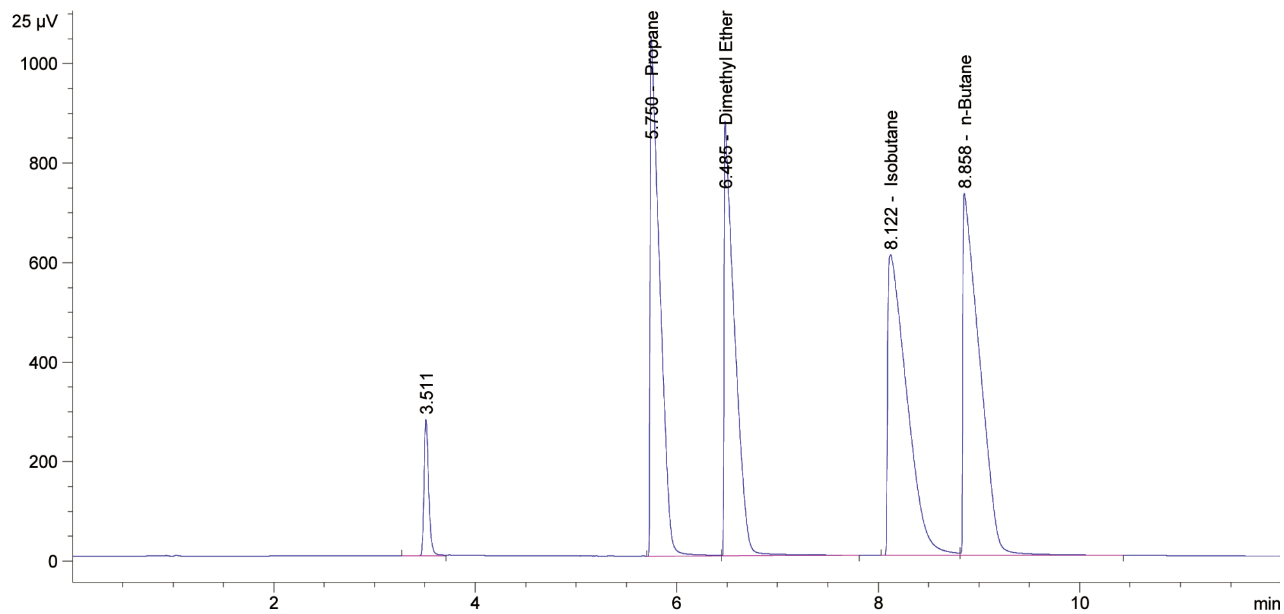

Figure 2. Chromagram of propane, dimethyl ether, isobutane, n-butane.

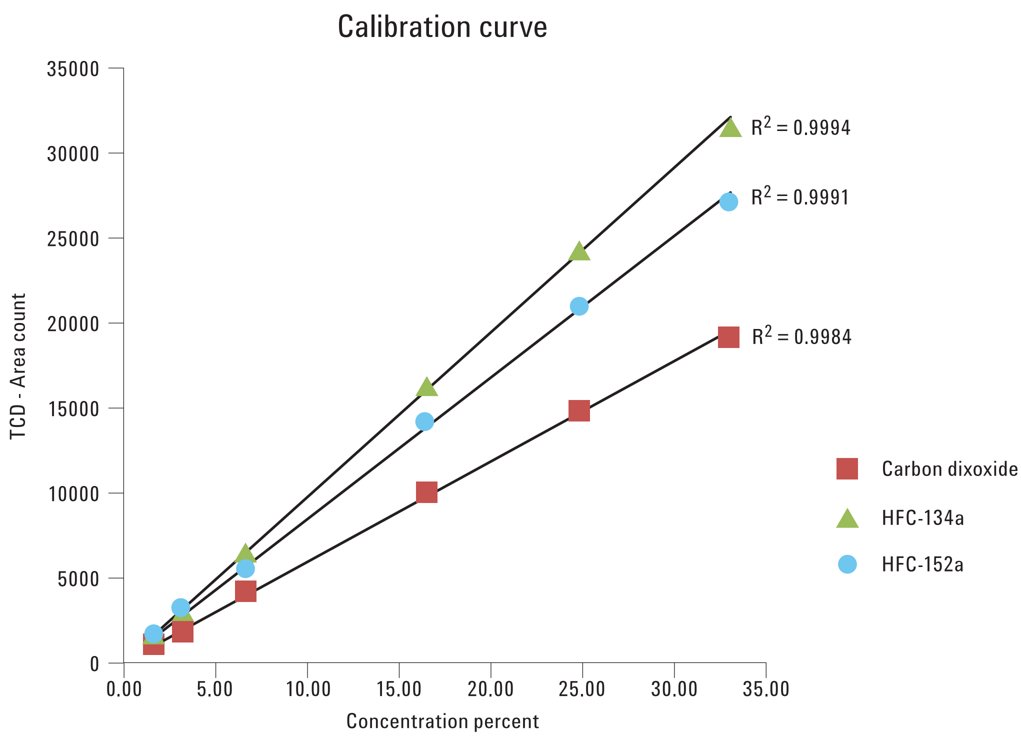

Figure 3. Six point calibration curve from 1.65% to 33% for Carbon Dioxide, HFC-134a, and HFC-152a. Split ratio range from 1:1 to 47:1.

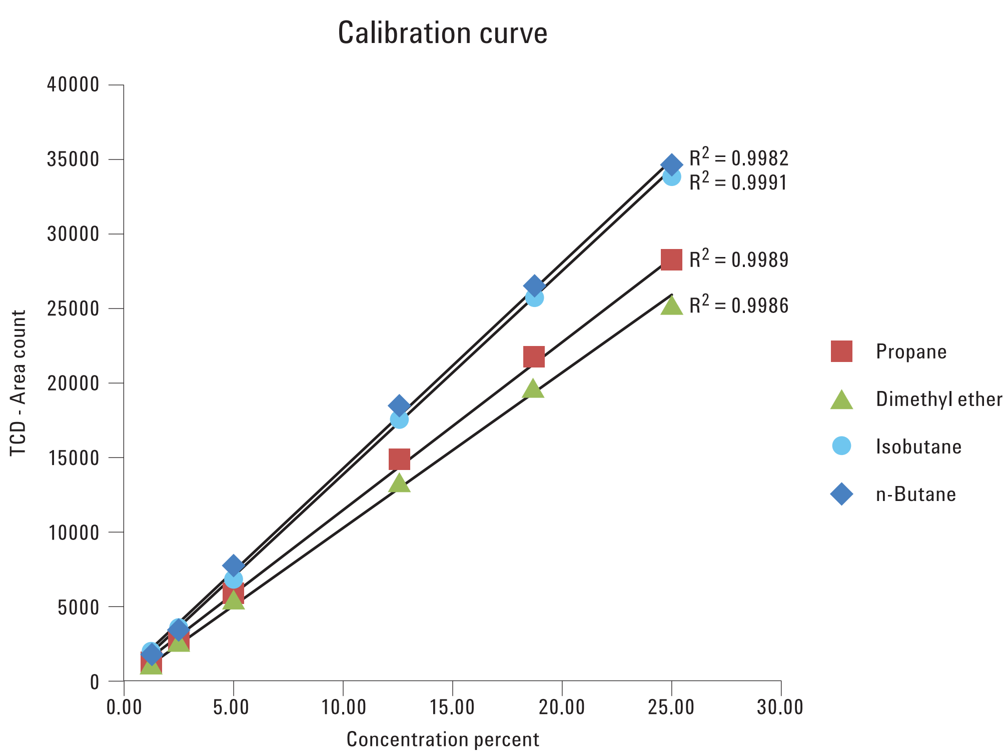

Figure 4. Six point calibration curve from 1.25% to 25% for propane, dimethyl ether, iso-butane, n-butane. Split ratio range from 1:1 to 47:1.

Conclusion

Analysis of consumer propellants can be achieved using a basic Agilent GC configured with a gas sample valve, split inlet, HP-PLOT Q column, and a TCD detector. The split inlet can be used to dynamically dilute samples. This is useful when a multipoint calibration is needed across a fairly narrow range of analysis. It was observed that split ratios up to 600:1 could produce very linear results.

References

1. Aerosol Propellants, The Alliance for Responsible Atmospheric Policy, April 12, 2011, http://www.arap.org/docs/aerosol.html

2. California Environmental Protection Agency Air Resource Board, Special Analysis Section Northern Laboratory Branch Monitoring and Laboratory Division, October 17, 2003, Standard Operating Procedure for the Determination of Exempt Compounds in Aerosol Consumer Product Propellant by Gas Chromatography, Revision 2.1

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
June 3, 2011
5990-8068EN

Agilent Technologies