Fast Analysis of Non-Traditional Gasoline Additives with Gas Chromatography – Vacuum Ultraviolet Spectroscopy

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Non-traditional gasoline additives (NTGAs) are being researched as beneficial octane-booster replacements for ethanol and methyl tert-butyl ether. Other octane-enhancing NTGAs, including acetone and N-methylaniline which can degrade automobile engine performance, are sometimes used illegally in gasolines outside the United States and Europe. Unfortunately, monitoring programs relying on ASTM D6730 (detailed hydrocarbon analysis) and ASTM 6839 (multidimensional gas chromatography) do not include most NTGAs in their scope. Gas chromatography (GC) with vacuum ultraviolet spectroscopy (VUV) offers an easy way to spectrally identify and quantify NTGAs in gasoline in under 34 minutes.

1. Introduction:

During the fuel refining process, various additives are blended into the fuel stream to adjust the fuel's properties. Properties of interest include vapour pressure [1,2], exhaust emission content [3], water tolerance [4], and corrosiveness [5], among others. Many of these additives are used in a range of concentrations, from bulk down to trace levels, depending on the compounds. One particular property affected by additive content is the octane rating, or octane number. The octane rating is a fuel's ability to resist 'knocking' or 'pinging' as a result of premature combustion [6]. Modern vehicles are designed to operate with fuel at a specific octane rating; for example, most light duty cars and trucks are designed to use fuel with an octane rating of 87, which can be found at most gas stations [7].

Many 'traditional' additives, such as benzene, toluene, ethylbenzene, and xylenes (BTEX) have been used to boost the octane rating [8,9]. However, these compounds are heavily regulated, forcing oil refineries to search for renewable and environmentally-friendly additives. Over the last two decades, ethanol has become an increasingly popular additive, and it is now blended at approximately 10% by volume in many gasolines [8]. Ethanol has many desirable properties, such as high biodegradability, low toxicity, and efficient burning [10]. However, it contains less energy per gallon than gasoline [11], and the increased requirements for crops such as corn would drive up food prices [12], so using too much ethanol in gasoline is not desirable.

Recently, research has been dedicated to using new 'non-traditional' gasoline additives (NTGAs) as viable additions to fuel blends [7,13]. For example, one study determined that ethyl acetate may be used as a beneficial octane-boosting compound that provides desirable properties, such as increased water tolerance [1]. Another study demonstrated a procedure for obtaining various furan compounds from pineapple plantation waste residues which could be used in gasoline [14].

While many NTGAS are beneficial and used ethically, several harmful, illegal additives have been found in gasoline. The Asian Clean Fuels Association (ACFA) identified octane-boosting additives that have undesirable side effects. Compounds such as acetone and dimethoxymethane (methylal) can cause swelling of plastic engine components, potentially leading to engine damage. Other harmful NTGAs may have negative effects on gasoline, including volatility, gum formation, and corrosion [15].

As the content of gasoline changes with advancing fuels technology, gasoline regulatory procedures must incorporate proper analytical techniques to analyse NTGAs. Currently, gasoline is analysed using methods such as ASTM D6730 (detailed hydrocarbon analysis, or DHA) or ASTM D6839 (multidimensional gas chromatography) [16,17]; however, these methods don't include most NTGAs within their scope. Due to the nature of these techniques, NTGAs may prove problematic. NTGAs in gasoline may coelute with known compounds in a DHA, but because DHA cannot provide spectral or structural information, quantitation may be affected [18]. Additionally, techniques like multidimensional GC may require changes in the analysis mode to properly analyse the NTGAs, increasing the complexity of the analysis [19].

A recently developed technique, gas chromatography - vacuum ultraviolet spectroscopy (GC-VUV), has proven to be a powerful alternative to traditional methods of gasoline analysis. Molecules eluting from the GC are exposed to light in the VUV range (125-240 nm), and because nearly every compound absorbs strongly in this range, compounds can be identified by their unique spectral fingerprints and quantified according to Beer-Lambert Law principles. Additionally, coeluting compounds can be distinguished by spectral

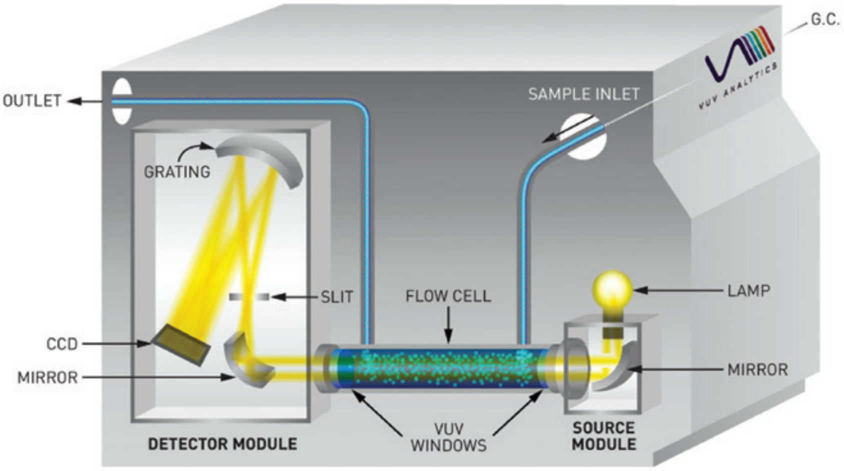


Figure 1a

Figure 1: a) Schematic of VUV spectrometer. Compounds eluting from the GC column are introduced to VUV-range light in the flow cell, and the resulting absorbance spectrum is recorded. b) Example spectra of a seven-carbon paraffin (heptane), isoparaffin (2-methylhexane), olefin (3-methyl-1-hexene), naphthene (methylcyclohexane), and aromatic (toluene). c) Example spectra of six closely-related aromatics. Each compound has a unique spectrum, but because they are all aromatics, they share the same aromatic spectral shape.

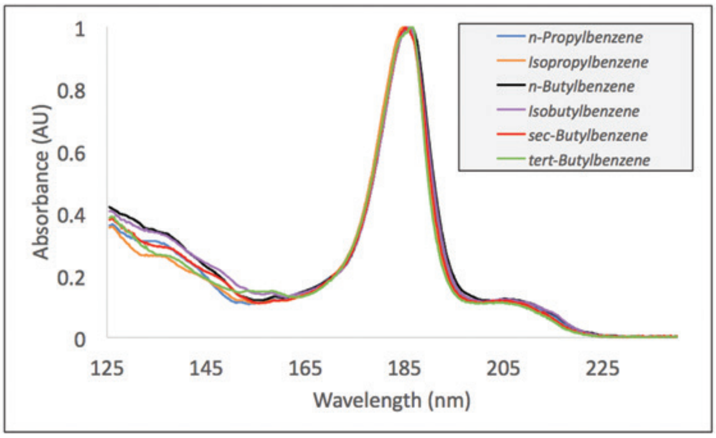


Figure 1b

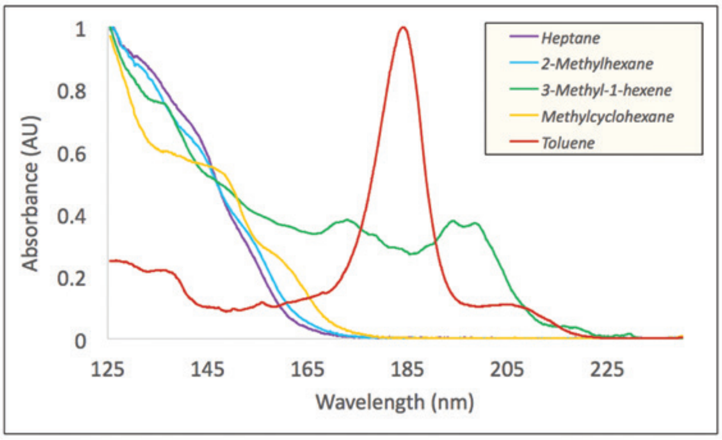


Figure 1c

deconvolution, allowing for additional chromatographic flexibility [20]. ASTM D8071 uses GC-VUV to analyse the paraffin/isoparaffin/olefin/naphthene/aromatic (PIONA) and oxygenate content of fuels samples in a single run, and because it uses a simple setup with a run time under 34 minutes, it is an ideal solution for fuels analysis [21].

This study aims to demonstrate GC-VUV's ability to analyse gasoline samples containing NTGAs. Rather than tailoring the method conditions to the new compounds, information on each NTGA was simply added to the spectral library and the samples were analysed using the method conditions listed in ASTM D8071 [21].

2. Experimental:

All samples were analysed with an Agilent 6890 gas chromatograph (Wilmington, DE, USA) paired with a VUV Analytics VGA-100 spectrometer (Cedar Park, TX, USA). The GC was equipped with a Restek Rxi-1ms column (Bellefonte, PA, USA) with dimensions of 30m x 0.25 mm ID x 0.25 µm and a Restek Topaz 4mm ID Precision inlet liner with wool. Helium with a purity of 99.999% was used as the carrier gas for the GC. Nitrogen with a purity of 99.999% was used as the makeup gas for the spectrometer.

All samples were run under the conditions specified by ASTM D8071 as follows:

Gas chromatograph

- Constant flow mode: 1.0 mL/min He
- GC inlet: 250°C, split 300:1
- Injection volume: 1 µL
- Oven: 35°C (10 min), 7°C/min to 200°C

VGA-100

- Makeup gas: 0.25 psi N2
- Acquisition range: 125-240 nm
- Acquisition rate: 4.5 Hz
- Transfer line temperature: 275°C
- Detector flow cell: 275°C

Oxygenate-free gasoline was obtained from Valero (San Antonio, TX, USA), and E10 gasoline (containing 10% ethanol) was obtained from a local gas station. All NTGA compounds and other reagents were purchased from Sigma Aldrich (St. Louis, MO, USA) with a purity of >99%. Each compound analysed as an NTGA is listed in Table 1.

Table 1: Thirty NTGA compounds with the respective structures. These compounds include a variety of oxygenates and other compounds that may be found in gasoline.

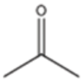
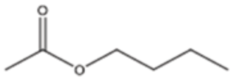
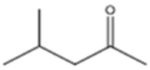
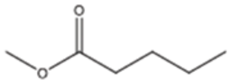
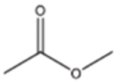
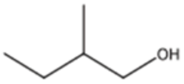
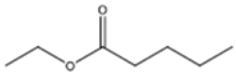
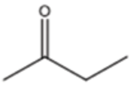
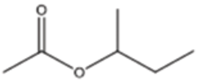
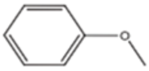
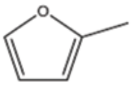
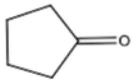
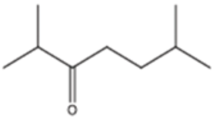
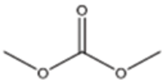
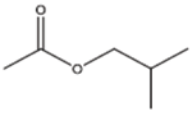
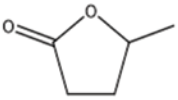
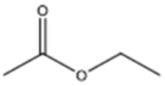
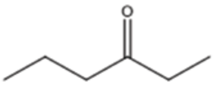
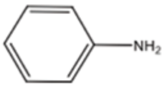
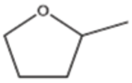
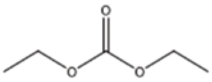
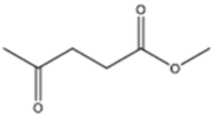
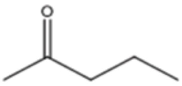
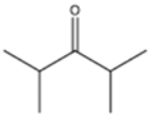
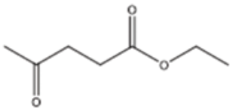
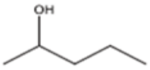
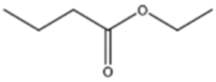
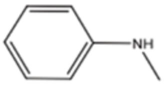
Acetone		2,5-Dimethylfuran		n-Butyl Acetate	
Dimethoxymethane		4-Methyl-2-Pentanone		Methyl Pentanoate	
Methyl Acetate		2-Methyl-1-Butanol		Ethyl Pentanoate	
2-Butanone		sec-Butyl Acetate		Anisole	
2-Methylfuran		Cyclopentanone		Isobutyl Isobutyrate	
Dimethyl Carbonate		Isobutyl Acetate		gamma-Valerolactone	
Ethyl Acetate		3-Hexanone		Aniline	
2-Methyltetrahydrofuran		Diethyl Carbonate		Methyl Levulinate	
2-Pentanone		2,4-Dimethyl-3-Pentanone		Ethyl Levulinate	
2-Pentanol		Ethyl Butanoate		n-Methylaniline	

Table 2: Relative response factors (RRF) and standard non-polar retention indices (RI) used for each NTGA.

Compound	Relative Response Factor (RRF)	Retention Index (RI)	Compound	Relative Response Factor (RRF)	Retention Index (RI)
Acetone	0.680	471	Isobutyl acetate	0.850	754
Dimethoxymethane	0.980	508	3-Hexanone	0.805	765
Methyl acetate	0.900	511	Diethyl carbonate	0.950	762
2-Butanone	0.740	575	2,4-Dimethyl-3-pentanone	0.790	779
2-Methylfuran	0.380	594	Ethyl butanoate	0.850	784
Dimethyl carbonate	1.050	563	n-Butyl acetate	0.850	796
Ethyl acetate	1.050	600	Methyl pentanoate	0.830	808
2-Methyltetrahydrofuran	0.950	669	Ethyl pentanoate	0.875	882
2-Pentanone	0.740	667	Anisole	0.285	902
2-Pentanol	0.830	687	Isobutyl isobutyrate	0.840	900
2,5-Dimethylfuran	0.390	697	Gamma-valerolactone	0.940	917
4-Methyl-2-Pentanone	0.670	722	Aniline	0.250	954
2-Methyl-1-butanol	0.875	723	Methyl levulinate	0.825	948
sec-Butyl acetate	0.900	745	Ethyl levulinate	0.805	1024
Cyclopentanone	0.800	764	N-Methylaniline	0.280	1041

*Table 3: Averaged observed volume % values for each NTGA in oxygenate-free gasoline at spikes of 1%, 3%, 5%, and 10% v/v. With the exception of gamma-valerolactone, all compounds demonstrated a high degree of linearity. *Because gamma-valerolactone was not soluble at 10% v/v in oxygenate-free gasoline, it was re-analysed in E10 gasoline, whose ethanol content allowed it to dissolve.*

Compound	Retention Time (min)	10% Spike	5% Spike	3% Spike	1% Spike	R^2
Acetone	2.65	10.9	4.96	3.00	0.956	0.998
Dimethoxymethane	2.83	10.4	5.12	3.13	1.08	>0.999
Methyl acetate	2.85	10.4	5.20	3.14	1.06	>0.999
2-Butanone	3.33	10.4	5.12	3.09	1.11	>0.999
2-Methylfuran	3.55	10.2	5.24	3.17	1.05	>0.999
Dimethyl carbonate	3.61	10.5	5.21	3.09	1.05	>0.999
Ethyl acetate	3.63	10.3	5.65	3.66	1.25	0.997
2-Methyltetrahydrofuran	4.61	10.2	5.13	3.13	1.04	>0.999
2-Pentanone	4.83	10.6	5.32	3.18	1.01	>0.999
2-Pentanol	5.39	10.2	5.19	3.32	1.15	>0.999
2,5-Dimethylfuran	5.69	10.2	5.18	3.18	1.03	>0.999
4-Methyl-2-Pentanone	6.62	10.3	5.30	3.19	1.06	>0.999
2-Methyl-1-butanol	6.97	10.3	5.38	3.21	1.08	0.999
sec-Butyl acetate	7.83	10.5	5.43	3.25	1.08	>0.999
Cyclopentanone	8.33	10.1	5.18	3.14	1.00	>0.999
Isobutyl acetate	8.60	10.5	5.40	3.20	1.04	>0.999
3-Hexanone	8.87	10.0	5.25	3.25	1.09	>0.999
Diethyl carbonate	8.95	10.5	5.36	3.18	0.954	>0.999
2,4-Dimethyl-3-pentanone	9.66	10.1	5.15	3.18	1.08	>0.999
Ethyl butanoate	10.35	10.0	5.22	3.19	1.06	0.999
n-Butyl acetate	11.16	10.2	5.27	3.16	1.06	>0.999
Methyl pentanoate	11.70	10.1	5.17	3.13	1.03	>0.999
Ethyl pentanoate	15.33	10.3	5.37	3.31	1.18	>0.999
Anisole	15.55	10.1	5.16	3.03	1.04	>0.999
Isobutyl isobutyrate	15.99	10.0	5.12	3.13	1.04	>0.999
Gamma-valerolactone (in Oxygenate-Free Gasoline)	16.01	6.71	5.02	3.08	1.00	0.917
Gamma-valerolactone (in E10 Gasoline)*	16.01	10.3	5.51	3.26	1.05	0.998
Aniline	17.39	10.3	5.23	3.19	1.07	>0.999
Methyl levulinate	17.59	10.2	5.13	3.19	1.10	>0.999
Ethyl levulinate	19.79	10.2	5.20	3.16	1.06	>0.999
N-Methylaniline	20.01	10.3	5.32	3.28	1.08	>0.999

Individual solutions of each NTGA were prepared by dissolving each compound in oxygenate-free gasoline at concentrations of 10%, 5%, 3%, and 1% v/v and analysed in triplicate. One compound, gamma-valerolactone, was not soluble at 10% in oxygenate-free gasoline, so it was dissolved in E10 gasoline at concentrations of 10%, 5%, 3%, and 1% v/v and analysed in triplicate. Additionally, individual solutions of three compounds - dimethoxymethane, 2,5-dimethylfuran, and N-methylaniline - were prepared with concentrations of 20%, 10%, 5%, 2%, 1%, 0.5%, 0.2%, 0.1%, and 0.05% v/v in E10 gasoline and again analysed in triplicate.

All data was processed using retention indices (RI) relative to methane and spectral matching. Quantification was achieved by comparing each compound's response to benzene and calculating a relative response factor (RRF). Procedures for determining RI and RRF values are listed in ASTM D8071 [21]. The RI and RRF values used in this experiment can be found in Table 2.

3. Results and Discussion:

The quantification results for each NTGA can be found in Table 3. Each compound of interest was quantified in gasoline over a range of 1% - 10% v/v.

While most NTGAs would likely fall between 1% and 10% v/v, this concentration range can be expanded. Three additives were chosen to be analysed over a range of 0.05% - 20% v/v and were analysed in triplicate. Those results can be found in Table 4.

Unlike methods such as DHA which rely on chromatographic separation to identify compounds through retention time, GC-VUV takes advantage of spectral deconvolution to compress the chromatography, giving a shorter run time of 34 minutes. While NTGAs may coelute with other compounds in gasoline, spectral deconvolution allows them to be identified and quantified without issue. For example, although acetone coelutes with isopentane under

Table 4: Average observed volume % values for dimethoxymethane, n-methylaniline, and 2,5-dimethylfuran at spikes of 20%, 10%, 5%, 2%, 1%, 0.5%, 0.2%, 0.1%, and 0.05% v/v. Even over a very extended concentration range, each compound demonstrated a high degree of linearity.

Compound	20% Spike	10% Spike	5% Spike	2% Spike	1% Spike
Dimethoxymethane	20.9	9.85	4.90	1.83	1.00
N-Methylaniline	22.8	11.2	5.62	2.20	1.11
2,5-Dimethylfuran	20.7	9.96	4.88	1.83	1.01

Compound	0.5% Spike	0.2% Spike	0.1% Spike	0.05% Spike	R^2
Dimethoxymethane	0.49	0.22	0.09	0.06	0.999
N-Methylaniline	0.54	0.22	0.07	0.03	0.999
2,5-Dimethylfuran	0.47	0.16	0.06	0.02	0.999

these conditions, it was quantified over the 1% - 10% v/v linear range with an R^2 value of 0.998. An example of spectral deconvolution can be seen in Figure 2. The spectral differences between acetone and isopentane allowed them to be distinguished and characterised separately despite their similar retention indices.

4. Conclusions

GC-VUV is able to successfully analyse and quantify several NTGAs in a 34-minute run time. These NTGAs can be uniquely identified by their spectral fingerprints, and spectral deconvolution allows these compounds to be identified and quantified even if they coelute with other compounds in gasoline. Highly linear data can be obtained for each NTGA over a wide range of concentrations without sacrificing the PIONA and oxygenate analysis necessary for fuel stream monitoring and regulation. Additionally, the ability to analyse these compounds without changing the hardware configuration or method parameters greatly simplifies the analysis, making it a desirable alternative to cumbersome methods such as ASTM D6730 or ASTM D6839.

Despite its advantages, NTGA analysis with GC-VUV is limited in part by the VUV spectral library. Unlike mass spectral libraries such as the one from NIST, which have been built over multiple decades, the VUV spectral library is relatively small. It contains entries for a large number of gasoline compounds and is continually growing, but many NTGAs may not exist in the library. If data is not available, unknown NTGA peaks may need to be identified with another technique, such as GC-MS. Once identified, a reference standard of the compound must be purchased and analysed so it can be included in the spectral library. However, once the compound is in the library, it can be analysed and quantified using GC-VUV as described in this paper.

5. References:

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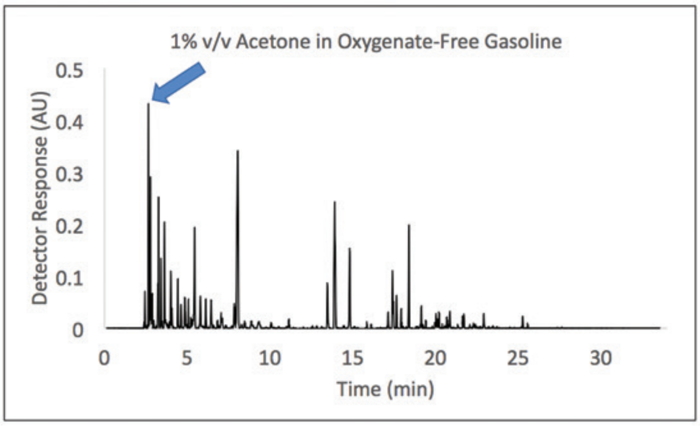

Figure 2a

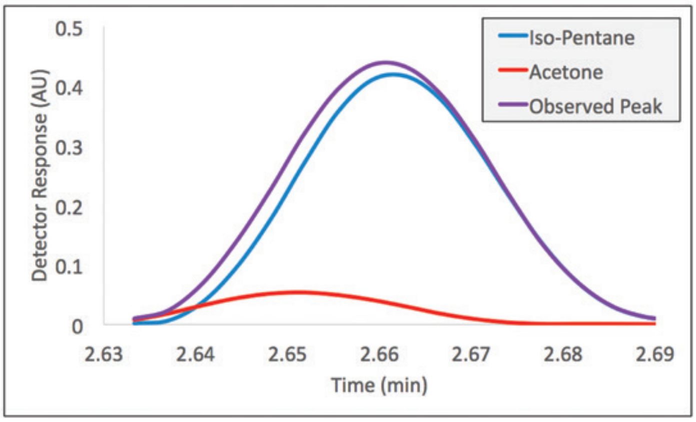

Figure 2b

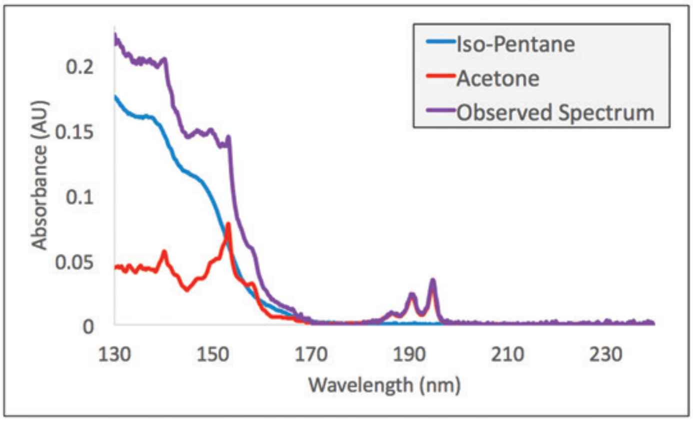

Figure 2c

Figure 2. a) Sample chromatogram of oxygenate-free gasoline containing 1% acetone v/v. Acetone and isopentane coelution is marked. b) Coelution of acetone and isopentane. Without spectral deconvolution, the acetone peak may have gone unnoticed under the isopentane peak; however, VUV can distinguish each compound and quantify them accurately. c) Observed spectrum at the coelution of acetone and isopentane. The observed spectrum has spectral features of both acetone and isopentane, and both compounds can be identified using VUV. d) Despite coeluting with isopentane, acetone can be quantified over the 1% - 10% v/v range with a high degree of linearity.

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