AUTOMATIC DETERMINATION OF TOTAL OXYGEN IN FUELS USING CO_2 COULOMETRY

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INTRODUCTION

Recently enacted clean air regulations require the addition of oxygenates to gasoline in certain areas of the United States. In addition, oxygenates are commonly used to increase octane number. Federal and some state regulations require that gasoline be tested for total oxygen content.

Gas chromatographic methods are time consuming and, since each oxygenate is determined individually, have a relatively poor accuracy since the error in each individual component is summed for the total oxygen content. Infrared methods are quite matrix dependent and therefore have limited applicability. The method presented here determines total oxygen by a pyrolysis-coulometric technique that provides rapid analysis and accurate determination of total oxygen that is useful for virtually all liquid fuels.

METHOD

An automated coulometric method based on the classical Schutze method has been developed for the determination of oxygen in fuels. Figure 1 shows a flow diagram of the analytical system and figure 2 shows the actual equipment. An autosampler using pressure to force the sample into the syringe, thereby preventing cavitation as in conventional syringe filling, is used. The sample is injected into a high temperature pyrolysis tube filled with catalyzed carbon. All oxygen in the sample is converted to CO. The CO produced from oxygen in the sample is scrubbed to remove potential interferences and is then oxidized with copper oxide in a low temperature furnace to convert the CO to CO_2. The CO_2 is quantitatively detected in a CO_2 coulometer. The CO_2 coulometer does not require sample calibration so the efficiency of the complete analytical system can be monitored and controlled. The coulometer is interfaced with a printer or computer to record the analytical data produced.

RESULTS & DISCUSSION

Table 1 shows results obtained on fuel samples prepared by adding the shown amount of laboratory grade oxygenate. The maximum RSD at the regulatory level (2.7% O) is less than 0.4% and recoveries were between 97 and 102%. The run time was six minutes and no standardization calibration was performed on the system.

Table 2 shows results obtained on oxygenated fuel samples prepared by outside sources. The baseline sample is a sample found to have negligible oxygen content. The three commercial standards were prepared by a third party to calibrate oxygen determination on usual commercial blends. The research mixtures were prepared by an oil company as possible oxygenate blends. The NIST standards were obtained from NIST as a certified standard for oxygenates in gasoline.

Pure MTBE was analyzed showing the applicability of the method to pure oxygenates.

CONCLUSIONS

The pyrolysis-coulometric procedure for total oxygen in fuels provides a rapid (<6 min.) precise (RSD <1%), accurate (recovery of 97-102%), and easy to use (no sample calibration) method for determining total oxygen in fuels.

Advantages of the new apparatus which is now commercially available include:

- Throughput of over 200 samples per day.
- Total oxygen (not specific oxygenated compounds)is determined.
- The coulometric detection is absolute so sample calibration is not required.
- Autosampler uses pressure to force sample into syringe, thereby preventing cavitation.
- Low maintenance.
- Applicable to a wide variety of liquid fuels.
- Continuous operator attention is not required.

TABLE 1

Results obtained with Samples of Prepared Oxygenates using Laboratory Reagents Prepared at 50%, 100% and 200% of the Regulatory Level

	Percent Oxygen		SD of	%
Oxygenate	Theory	Ave. Result	Triplicate Run	Recovery
Methanol	1.03	1.00	0.006	97.1
	2.81	2.75	0.010	97.9
	5.08	5.01	0.006	98.6
Ethanol	0.99	1.01	0.006	102.0
	2.78	2.75	0.006	98.9
	3.50	3.49	0.006	99.7
Isopropanol	1.02	1.01	0.006	99.0
	2.81	2.79	0.006	99.3
	4.96	4.91	0.015	99.0
MTBE	1.02	1.04	1.010	102.0
	2.74	2.73	0.000	99.6
	4.85	4.82	0.006	99.4

TABLE 2

Results Obtained on Various Samples from Third Party Sources

Sample	% Found	% Theory	% Recovery
Baseline	0.00	0.00	--------
Commercial Std. #1	2.50	2.50	100.0
Commercial Std. #2	2.74	2.76	99.3
Commercial Std. #3	5.11	5.16	99.0
Research #1[1]	4.69	4.73	99.1
Research #2[2]	3.80	3.83	99.2
NIST 1837	6.55	6.59	99.4
NISR 1838	3.97	3.96	100.2
MTBE	13.28	13.36	99.4

[1] Contains TAME, MTBE, t-pentanol, t-butanol, ethanol, and methanol.

[2] Contains ETBE, t-butanol, sec-butanol

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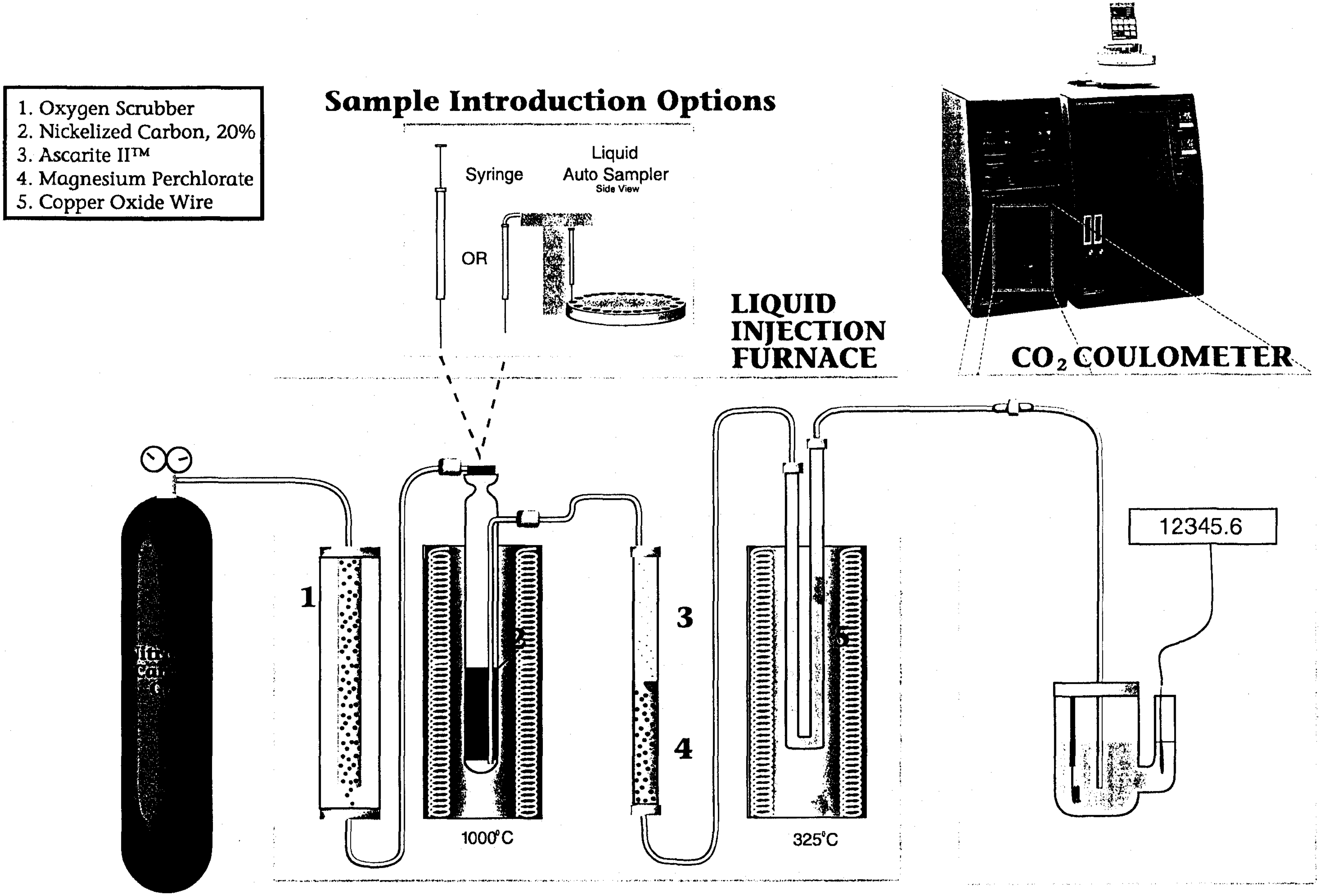
1. Oxygen Scrubber
2. Nickelized Carbon, 20%
3. Ascarite II™
4. Magnesium Perchlorate
5. Copper Oxide Wire
Sample Introduction Options
Syringe
OR
Liquid Auto Sampler
Side View
LIQUID INJECTION FURNACE
CO₂ COULOMETER
1
2
3
4
5
1000°C
325°C
12345.6

Figure 1

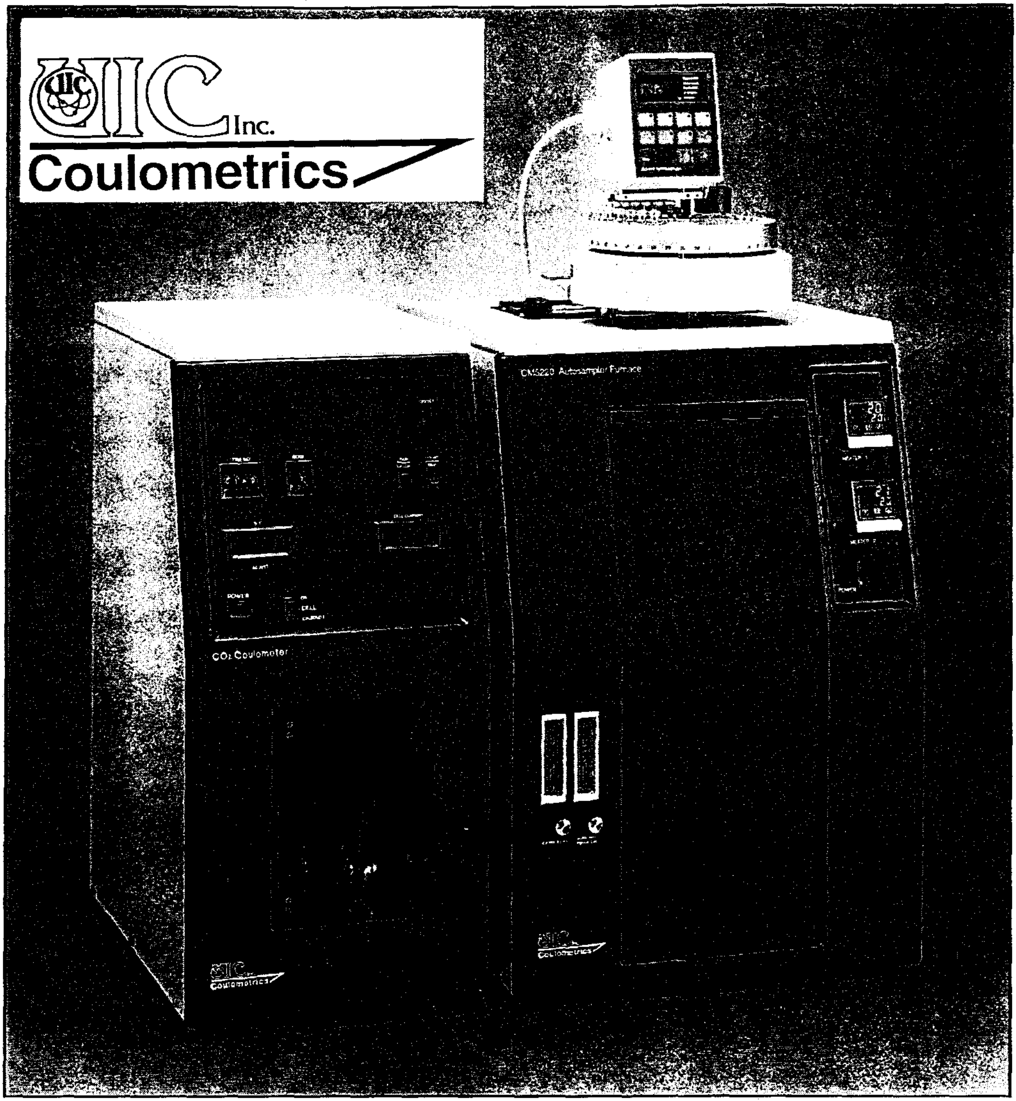
UIC Inc.
Coulometrics
CO₂ Coulometer
CM5220 Autosampler Furnace
POWER
CELL
UIC Coulometrics
UIC Coulometrics

Figure 2

originals

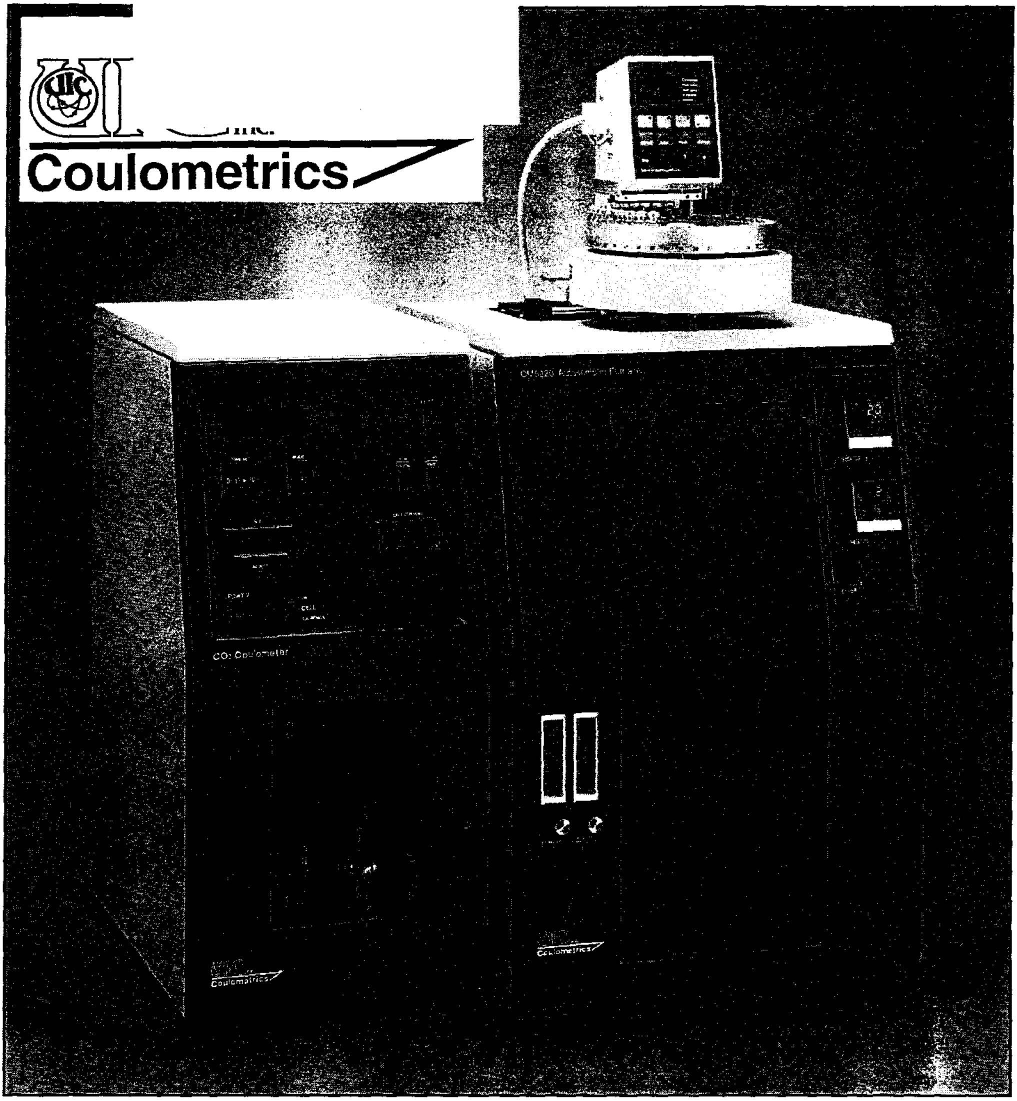

Figure 2