

Introduction

The analysis of ethanol has become an important issue because of the increasing use of ethanol/gasoline blends. The presence of heavy metal traces in car fuels can affect engine performance. Copper, for example, is a very active catalyst for the low-temperature oxidation of hydrocarbons. Consequently, copper concentrations above 12 µg/kg in commercial gasoline are expected to promote the deterioration of olefins and the formation of gum. The monitoring of heavy metal traces in car fuels is therefore of crucial importance.

In this work, ethanol/gasoline blends (E85, 85% ethanol + 15% gasoline) are analyzed for copper by anodic stripping voltammetry (ASV). ASV is a sensitive and selective electroanalytical technique comprising two steps:

- metal ions are electrodeposited on the mercury electrode, which is held at a suitable potential
- the (amalgamated) metal deposits are anodically stripped from the mercury electrode by scanning the potential.

The ASV is performed using the hanging mercury drop electrode (HMDE) and the 797 VA Computrace for trace analysis. The HMDE is used with a platinum auxiliary electrode and an Ag/AgCl reference electrode using saturated lithium chloride in ethanol as the inner electrolyte.

The concentration of the copper in the samples is quantified by standard addition.

System setup



Voltammetric parameters

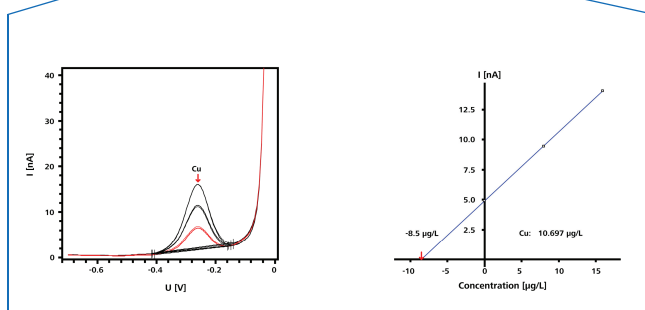
Voltammetric parameters were optimized in preliminary experiments.

Working electrode	HMDE
Mode	DP
Deposition	potential -700 mV
	time 60 s
Potential	start -700 mV
	end 0 mV
Sweep rate	20 mV/s

Spike recovery

Measuring solutions consisted of 10 mL analytical grade ethanol, 2.5 mL LiCl solution and 50 µL HCl. The performance of the method was evaluated by the analysis of copper-spiked measuring solutions (5, 10, 20, 50 and 100 µg/L).

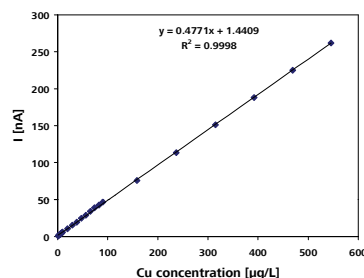
	Spiked Cu concentration [µg/L]														
	5			10			20			50		100			
Measured [µg/L]	4.95	5.75	6.05	9.62	10.75	9.6	20	19.53	18.12	52.6	47.4	49.4	105.15	98.2	103.4
Mean value [µg/L]	5.58			9.99			19.22			49.8		102.2			
Recovery [%]	111.7			99.9			96.1			99.6		102.2			
RSD	8.3%			5.4%			4.2%			4.3%		2.8%			



Within a concentration range of 10...100 µg/L, recovery rates for copper in ethanol ranged between 96 and 103%. At the lower concentration level (5 µg/L), copper recoveries of approx. 112% were obtained.

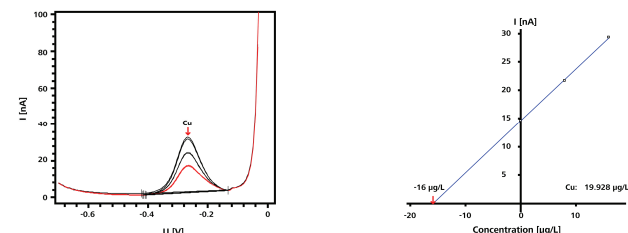
Employing a preconcentration time of 60 s, the limit of detection (LOD) was determined as 2 µg/L copper, complying with the minimal requirements of ASTM D 4806 and prEN 15376 (both 10 µg/L). The effect of added denaturing agents (2% diisopropyl ether and isopropanol) was negligible.

Calibration



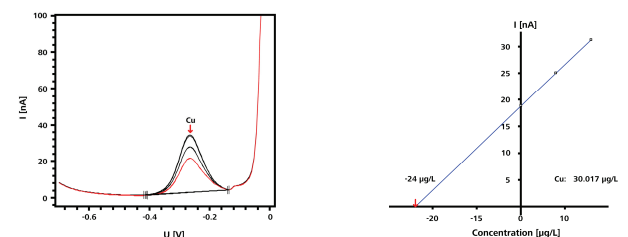
Cu in an ethanol/gasoline blend (E85)

a) E85 sample



The copper concentration in the E85 ethanol/gasoline blend was 20 µg/L.

b) E85 sample spiked with 10 µg/L copper



For the E85 sample (20 µg/L), spiked with 10 µg/L copper, a recovery rate of 100% was observed.

Summary

The presence of copper in fuel ethanol blends has gained considerable attention, since Cu²⁺ catalyzes oxidative reactions in gasoline leading to a deterioration of olefins and the formation of gum.

Anodic stripping voltammetry (ASV), one of the most sensitive and accurate techniques for trace-metal analysis, has been demonstrated for the determination of Cu(II) in ethanol/gasoline blends without any sample pretreatment. Copper ions are first electrodeposited onto the surface of a hanging mercury drop electrode (HMDE) before the amalgamated copper is quantitatively stripped (anodically dissolved), a current-voltage curve being recorded.

Experimental conditions such as deposition time and potential as well as the adequate electrolyte and reference electrode were determined in preliminary experiments. For synthetic samples spiked with Cu²⁺ (5...100 µg/L), recovery rates between 96 and 112% were obtained. The copper-spiked E85 sample provided a recovery of 100%. The relative standard deviations for Cu²⁺ concentrations of 5 µg/L and above were 8.0 and 5.5%, respectively. Using a preconcentration time of 60 s at -0.7 V versus Ag/AgCl, a linear range of 0...500 µg/L with a detection limit of 2 µg/L was obtained.