Determination of hazardous substances in electrical and electronic equipment

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Voltammetry

Ion Chromatography

Summary

The Restriction of Hazardous Substances (RoHS) Directive 2002/95/EC stipulates maximum limits for the hazardous metals cadmium, lead and mercury as well as the hexavalent chromium and the brominated flame retardants in electrical and electronic products. To ensure compliance, reliable analysis methods are required.

This poster deals with the wet-chemical determination of trace concentrations of the six RoHS-restricted substances in a wide variety of materials including metals, electrotechnical components, plastics and wires. After sample preparation according to IEC 62321, the metals lead, cadmium and mercury are best determined by anodic stripping voltammetry (ASV) and the flame retardants PBB and PBDE are quantified by direct-injection ion chromatography (IC) using spectrophotometric detection. Chromium(VI) can be determined either by adsorptive stripping voltammetry (AdSV) or IC. Both methods are very sensitive and meet prescribed RoHS limits.

Regarding the halogen-free initiative, the presentation describes the alternative determination of trace halides in non-aqueous sample matrices by combustion IC.

Introduction

As technology advances, the volume of electronic waste (e-waste) is steadily growing. In Europe, the ever-growing pile of unwanted, obsolete, or unusable electronic products such as computers, TV sets, stereo equipment, etc. grows at a rate of 3...5% per annum, three times the rate of the municipal waste stream. Electronic waste mainly consists of the bulk material such as iron, aluminum and plastics as well as smaller quantities of hazardous heavy metals and/or polybrominated flame retardants. Since more and more e-waste ends up in landfills and incinerators, toxic substances are increasingly released into the environment and pose serious health risks and environmental dangers.

In Europe, the directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment 2002/95/EC, commonly referred to as RoHS, came into effect in 2006. With some exceptions, new electric and electronic products must not exceed stipulated levels of lead, cadmium, mercury, hexavalent chromium as well as the polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs). In other parts of the world similar directives are under way. In order to comply with these regulations, manufacturers have to determine the heavy metal and polybrominated flame retardant contents of their products.

Instrumentation

Voltammetry

- 797 VA Computrace

Ion chromatography

UV/VIS detection

- 844 UV/VIS Compact IC
- 863 Compact IC Autosampler
- Post-Column Reactor (not shown)

Combustion IC

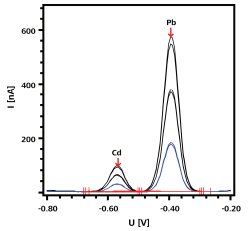
- 881 Compact IC pro – Anion – MCS
- MultiTek Combustion IC

Voltammetry

Lead and cadmium

Example: metals

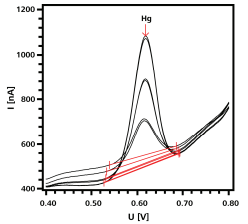
Sample preparation	according to IEC 62321
Electrolyte	0.01 mol/L ammonium oxalate, pH = 2
Working electrode	Hanging Mercury Drop Electrode (HMDE)
Mode	Differential pulse
Deposition potential	– 850 mV
Deposition time	30 s
Start potential	– 800 mV
End potential	– 200 mV
Sweep rate	10 mV/s



Mercury

Example: metals

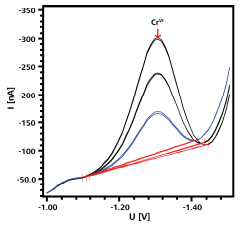
Sample preparation	according to IEC 62321
Electrolyte	3 mmol/L sodium chloride 2 mmol/L ethylenediaminetetraacetic acid (EDTA) 0.11 mol/L perchloric acid
Working electrode	Rotating Disc Electrode (RDE)
Mode	Differential pulse
Deposition potential	+ 370 mV
Deposition time	30 s
Start potential	+ 400 mV
End potential	+ 800 mV
Sweep rate	20 mV/s



Chromium(VI)

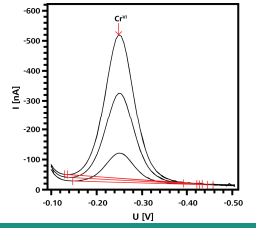
Example: chromate coatings

Sample preparation	according to IEC 62321
Electrolyte	0.04 mol/L sodium acetate 0.01 mol/L diethylenetriaminepentaacetate (DTPA) 0.5 mol/L sodium nitrate, pH = 6.2 ± 0.1
Working electrode	Hanging Mercury Drop Electrode (HMDE)
Mode	Differential pulse
Deposition potential	– 900 mV
Deposition time	30 s
Start potential	– 1000 mV
End potential	– 1500 mV
Sweep rate	33 mV/s



Example: polymer materials

Sample preparation	according to IEC 62321
Electrolyte	1 mol/L ammonia 0.5 mol/L ammonium chloride
Working electrode	Dropping Mercury Electrode (DME)
Mode	Differential pulse
Start potential	– 100 mV
End potential	– 500 mV
Sweep rate	10 mV/s

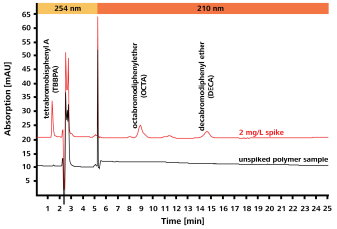


Ion chromatography

Halogenated compounds

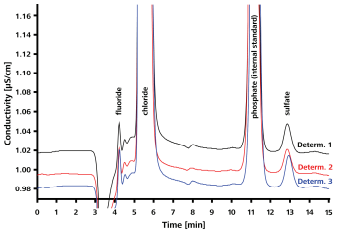
Polybrominated organic substances in polymers – UV/VIS detection

Sample preparation	according to IEC 62321
Column	Nucleosil EC-7-C18
Column temp.	25 °C
Eluent	97% methanol 3% phosphate buffer (pH = 7)
Flow	1.0 mL/min
Loop	20 µL
Wavelength	254 nm (TBBPA) 210 nm (OCTA und DECA)



Halogenated materials in PVC-containing cables – combustion IC

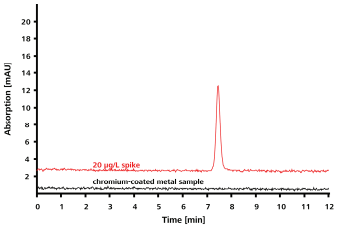
Sample preparation	combustion
Column	Metrosep A Supp 4 - 250/4.0
Column temp.	25 °C
Eluent	1.7 mmol/L sodium carbonate 1.8 mmol/L sodium hydrogen carbonate
Flow	1.0 mL/min
Loop	10 µL
Abs. solvent	30 mg/L hydrogen peroxide 1 mg/L phosphate (internal standard)



Chromium(VI) – UV/VIS detection

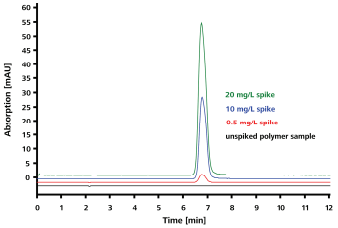
Example: chromate coatings

Sample preparation	according to IEC 62321
Column	Metrosep A Supp 5 -150/4.0
Column temp.	25 °C
Eluent	10 mmol/L sodium carbonate 1 mmol/L sodium hydrogen carbonate
Flow	0.7 mL/min
Loop	200 µL
PCR reagent	diphenylcarbazide
PCR flow	0.6 mL/min
Wavelength	540 nm



Example: polymer materials

Sample preparation	according to IEC 62321
Column	Metrosep A Supp 5 -150/4.0
Column temp.	25 °C
Eluent	10 mmol/L sodium carbonate 1 mmol/L sodium hydrogen carbonate
Flow	0.7 mL/min
Loop	20 µL
PCR reagent	diphenylcarbazide
PCR flow	0.6 mL/min
Wavelength	540 nm



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