Determination of ultratrace elements in liquid crystal

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Goal

To demonstrate the suitability of the Thermo Scientific™ Element 2™ High Resolution ICP-MS for trace metals analysis in high purity samples, related to the manufacture of semiconductors.

Summary

The Thermo Scientific™ Element 2™ High Resolution ICP-MS is used to determine sub-ng/g levels of metal contaminants in liquid crystal. The liquid crystal sample is dissolved (1:20 m/m) in an organic solvent (propylene glycol monomethyl ether, PGME) for analysis. Instrumental sensitivity in the organic diluent is identical to that in dilute nitric acid (> 1000 cps per pg/g In). High mass resolution is used for the analysis of ten of the fifteen elements determined due to the presence of matrix-induced polyatomic interferences. Detection limits in the PGME solvent are between 0.7 to 50 pg/g for the elements determined.

Introduction

Liquid crystal (LC) display technologies are increasingly moving towards large screen displays. Because the performance of the LC display is strongly influenced by trace element contamination introduced during the manufacturing process, a fast, reliable multi-element analysis technique capable of directly measuring low-ppt metal contaminants in LC samples is required.

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PGME ($CH_3OCH_2CHOHCH_3$) with a molecular weight of 90.1 g/mol and a 120 ˚C boiling point is commercially available at low trace metal concentrations for use in semiconductor applications and has been used as a diluent for the analysis of photo resist with the Element 2 HR-ICP-MS. In this report, it is shown that the Element 2 HR-ICP-MS with its high mass resolution, sensitivity and resistance to matrix effects can overcome all of these problems in the analysis of trace metal concentrations in LC with direct analysis after simple dilution in PGME solvent. Analytically determined concentration data will be reported as well as detection limits for the fifteen elements quantified.

Experimental

The sample introduction system used is listed below:

- 50 µL/min self-aspirating PFA concentric nebulizer

- PFA endcap with oxygen addition port

- PFA spray chamber

- Demountable quartz torch

- 1 mm ID sapphire injector

- Pt tipped sampling and skimmer cones

LC samples were diluted 1:20 (m/m) in high purity PGME solvent and were spiked with an internal standard (500 pg/g Rh) before analysis.

Results

Identification of polyatomic interferences

Prior to the routine analysis of any unknown sample, each element should be individually evaluated for interferences from matrix induced polyatomic species. With quadrupole ICP-MS, this evaluation can only be made indirectly: either by mathematical combination of major matrix components previously determined by other techniques, or by analysis of 'interference-check' standards. With High-Resolution ICP-MS, such analyses are unnecessary as the definitive existence of matrix-induced polyatomic interferences can be seen in a high resolution scan made across the element of interest.

An LC sample was prepared and all analysis elements were scanned for interferences in high resolution. For ten of the fifteen elements investigated, matrix induced interferences were identified that required the use of medium (R = 4000) or high (R = 10000) resolution in order to achieve interference free quantification (Table 1).

Table 1. Isotopes used for analysis and polyatomic interferences identified in the LC sample (diluted *20 in PGME).

Isotope	Interferences identified
^7Li	$^{14}N^{2+}$
^{24}Mg	$^{12}C_2$
^{27}Al	$^{12}C^{14}NH$, $^{13}C^{14}N$
^{39}K	^{38}ArH
^{44}Ca	$^{12}C^{16}O_2$, $^{28}Si^{16}O$
^{47}Ti	$^{31}P^{16}O$, $^{30}Si^{16}OH$
^{52}Cr	$^{40}Ar^{12}C$
^{55}Mn	$^{40}Ar^{15}N$, $^{40}Ar^{14}NH$
^{56}Fe	$^{40}Ar^{16}O$, $^{12}C_2{}^{16}O_2$
^{66}Zn	$^{38}Ar^{12}C^{16}O$

The polyatomic interferences observed in medium mass resolution under hot plasma conditions at the nominal mass of 56 are shown in Figure 1. The Fe peak at 55.935 amu is completely resolved from both the well-characterized $^{40}Ar^{16}O$ interference at 55.957 amu as well as a significant matrix induced interference from $^{12}C_2{}^{16}O_2$ at 55.990 amu using medium resolution (R = 4000). It is important to note that the use of high mass resolution allows straightforward separation of the elemental peak from all observed interferences with no change in instrument operating conditions and during the same scan.
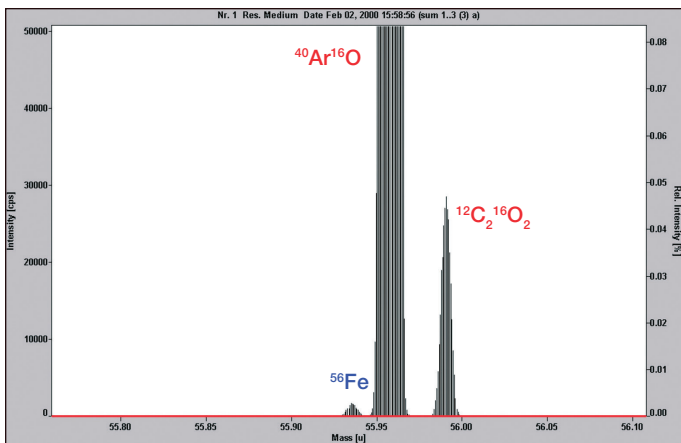
Figure 1. Mass spectrum around mass 56 in medium resolution. Apart from the ^{56}Fe peak being shown to be clearly resolved from the ^{40}Ar^{16}O interference, an additional interference from ^{12}C$_2$^{16}O$_2$ was also identified.

Sensitivity in the PGME diluent

The Element 2 HR-ICP-MS with a specified sensitivity of > 1 Mcps per ng/g In and detector dark noise of < 0.2 cps has been shown to be ideally suited for the determination of ultra-trace metal impurities in samples with simple matrices such as deionized water and IPA. To achieve comparable detection limits in the LC sample, sensitivity in the PGME solvent should be as high as that routinely obtained in less complicated matrices.

Figure 2 shows the Element 2 HR-ICP-MS sensitivity in a PGME solution spiked with 1 ng/g of a multi-elemental solution containing Li, In and U. Signal stability over the two minute analysis period is < 1% RSD. The operating parameters shown are those used for the LC analysis. There is no suppression caused by the PGME matrix; instrumental sensitivity in the solvent is identical to that in dilute nitric acid with > 1,000,000 cps per ng/g In.

Results

Fully quantitative analysis of fifteen elements in a sample of LC diluted 1:20 m/m in high purity PGME organic solvent was performed using a standard addition calibration in the sample matrix with spike concentrations of 5 to 1000 pg/g, depending on the concentration level of the element.

An internal standard (500 pg/g Rh) was added to all samples. Figure 3 shows the standard addition calibration line obtained for ^{52}Cr in medium resolution in the diluted LC matrix with standard additions at 5 and 10 pg/g.
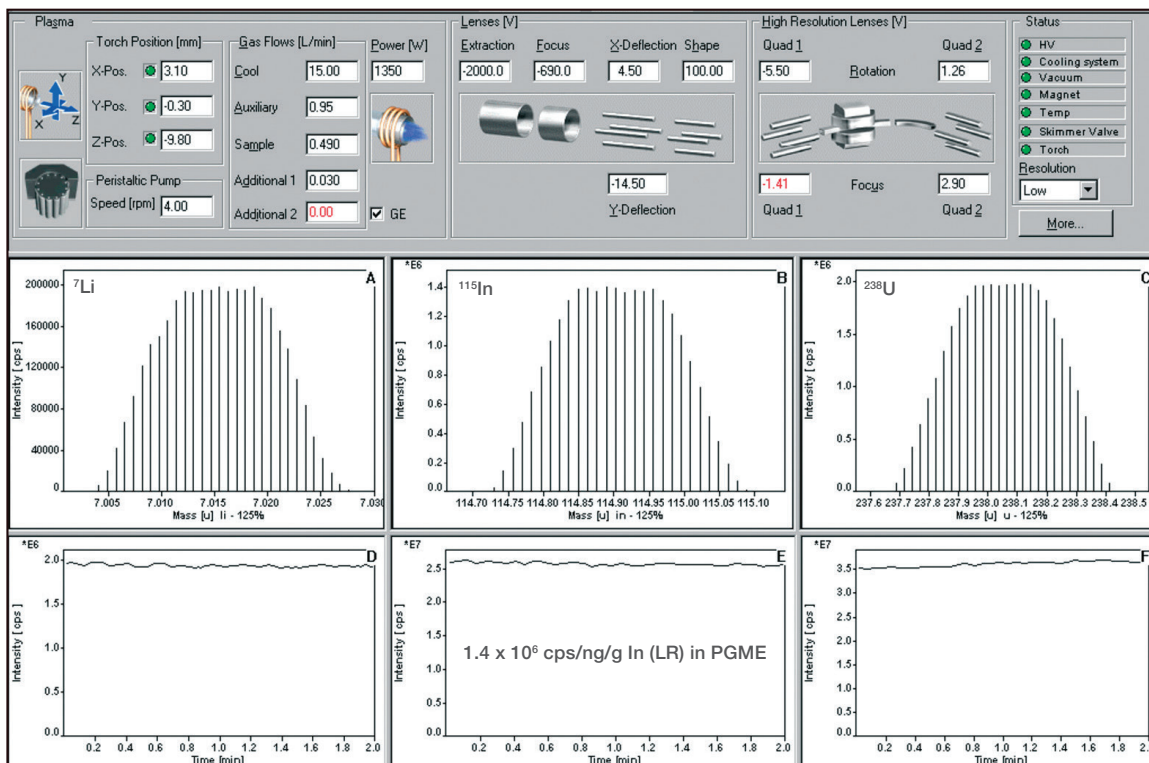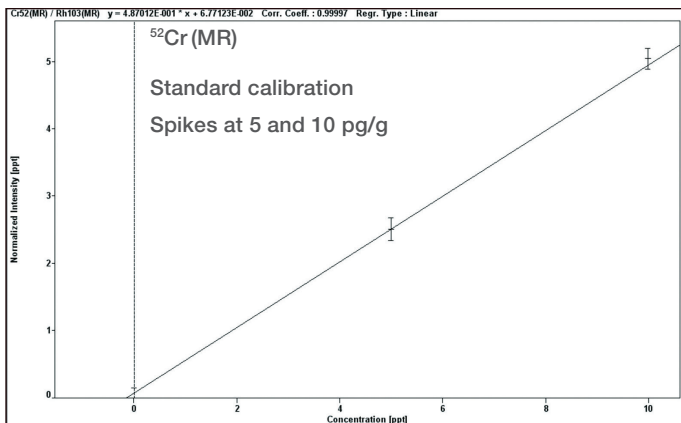

Figure 2. Sensitivity in the PGME matrix.

Figure 3. Calibration line for ^{52}Cr in the LC sample.

This calibration shows that sub-ppt concentrations can be directly quantified for ^{52}Cr in medium resolution in the diluted LC sample. Concentration data in both the diluted sample and in the LC after correction for dilution, as well as detection limits determined in the PGME solvent, are presented in Table 2.

Table 2: Concentration data for the LC sample (both diluted and after correction for dilution) as well as detection limits for the fifteen elements determined.

Isotope	R	Detection limit (pg/g)	Value in diluted solution (pg/g)	Dilution corrected (*20) final value (pg/g)
^{23}Na	LR	29	66	1320
^{60}Ni	LR	6.5	31	620
^{63}Cu	LR	5.5	29	580
^{118}Sn	LR	0.7	21	420
^{208}Pb	LR	8.1	485	970
^{7}Li	MR	3.0	< 3.0	< 60
^{24}Mg	MR	29	< 29	< 580
^{27}Al	MR	17	29	580
^{44}Ca	MR	50	497	9940
^{47}Ti	MR	15	< 15	< 300
^{52}Cr	MR	0.7	< 0.7	< 14
^{55}Mn	MR	0.9	3.9	78
^{56}Fe	MR	3.8	9.5	190
^{66}Zn	MR	11	21	420
^{39}K	HR	4.5	781	15620

Detection limits shown are calculated as the analyte concentration equivalent to three times the standard deviation from ten replicate on-peak analyses of the PGME blank. Detection limits are limited by sample purity.

Conclusions

Matrix-induced spectral interferences identified in the diluted LC sample are shown to require the use of high resolution ICP-MS for accurate low concentration level analysis. The use of medium resolution (R = 4000) is necessary for the analysis of ten of the fifteen elements determined (Li, Mg, Al, K, Ca, Ti, Cr, Mn, Fe and Zn). Because of the high sensitivity in high mass resolution of the Element 2 HR-ICP-MS, quantification is possible without desolvation. The analysis of all elements was performed without any reoptimization of instrument operating conditions and only required five minutes. The high sensitivity in the sample matrix and low dark noise count rate of the Element 2 HR-ICP-MS enable sub pg/g detection limits.

The combination of variable mass resolution (for identification and elimination of polyatomic interferences), automated addition of oxygen (for the combustion of carbon), an inert sample introduction system, high sensitivity with oxygen addition and resistance to matrix effects, show the Element 2 HR-ICP-MS to be ideally suited for the quantification of sub-ng/g concentrations of metals in liquid crystal.

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