High Resolution Accurate Mass (HRAM) GC-MS measurements for phthalates contamination assessment in wine

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INTRODUCTION

This poster shows a workflow solution of specialized Chromatography Consumables and High Resolution Accurate Mass (HRAM) GC-MS measurements for Phthalates contamination assessment in wine. A novel analytical method development is shown for the quantitative determination of phthalates in wine by using Thermo Scientific Orbitrap™ MS-based GC and a variety of different unique consumables.
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Phthalates (Phthalate Acid Esters, PAEs) have widespread use in the polymer industry as plasticizers and softeners to increase the plasticity of polymer materials and their toughness and strength. They are chemically inert, have high density, low to medium volatility, high solubility in organic solvents, and are easily released to the environment during aging of polymer materials.

Phthalate plasticizers migrate from plastic containers or closures into soft drinks and alcoholic beverages. PAEs released into the environment and food chain can act as hormones simulating the body's natural endocrine responses. They can potentially interfere with the normal role of hormones, and affect the body's most basic physiological control mechanisms. In Europe, phthalates concentration in wine and spirits is currently restricted according to Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials. The specific migration limit (SML) for wine and spirits is set at 0.3, 1.5 and 30 mg/L for DBP, DEHP and BBP, respectively.

Alcoholic beverages stored in plastic containers are at particular risk, due to their ethanol content which facilitates the PAEs solubility and their migration into the beverages from the plastic contact materials. The contamination risk therefore increases with liquors having high ethanol content.

In this study, the performance of the Thermo Scientific™ QExactive™ GC hybrid quadrupole-Orbitrap mass spectrometer (MS) has been evaluated for the accurate quantitative analysis of phthalates in wine samples. The QExactive GC Orbitrap MS provides high mass resolving power up to 120,000 (m/z 200) full width half maxima (FWHM) to facilitate highly accurate mass measurements. Besides, the system provides fast scan speeds and high intrascan dynamic range (>5000) to facilitate the detection of trace compounds in the presence of high content of matrix components.

METHOD

Standard solutions were prepared by fortifying wine blank extract to generate matrix matched calibration series. Recovery has been evaluated by spiking a blank wine sample at 500 ng/mL prior to extraction.
A procedural blank was also prepared by using n-Hexane.
The following PAEs have been included in the standard solutions:

- Bis-iso-decylphthalate (DIDP)
- Bis-butylphthalate (DBP)
- Benzylbutylphthalate (BBP)
- Bis-isononylphthalate (DINP)
- Bis-2ethylhexylphthalate (DEHP)
- Bis-n-octylphthalate (DNOP)
- D^4 DEHP used as internal standard

A calibration series was prepared from 0, 1, 5, 10, 100, 500, 1000, 10000 ng/mL in wine matrix extracted with n-Hexane and spiked post extraction.

Extraction procedure:

2 mL of wine were transferred into a 10 mL vial and the ethanol content was removed under nitrogen at 70 ° C.
Then, 1 mL of wine sample was added with 2 mL of Hexane. The samples were mixed with Vortex for 2 minutes and centrifuged for 5 minutes at 3000 rpm. An aliquot was transferred to a GC vial for analysis. Vials Total recovery vials have been used (PN: 1.2 UHRRV), crimped capped with foil closures (PN: 11-ACAL).

Instrument method:

A QExactive GC hybrid quadrupole- Orbitrap mass spectrometer was used. Sample introduction was performed by using a Thermo Scientific™ TriPlus™ RSH autosampler and the chromatographic separation was obtained by using a Thermo Scientific™ TRACE™ 1310 gas chromatograph (GC) equipped with the Thermo Scientific™ TraceGOLD TG-35SilMS™ 30 m × 0.25 mm I.D. × 0.25 µm film capillary column.

Fig 1. Instrument configuration

Table 1. Instrument Parameters

TRACE 1310 GC Parameters	
Injection Volume (µL):	1.0
Liner	SL Single tapered
Inlet (°C):	280
Inlet Module and Mode:	Splitless
Carrier Gas, (mL/min):	He, 1.2
Oven Temperature Program:	
Temperature 1 (°C):	80
Hold Time (min):	1.0
Temperature 2 (°C):	280
Rate (°C/min)	10
Hold Time (min):	10

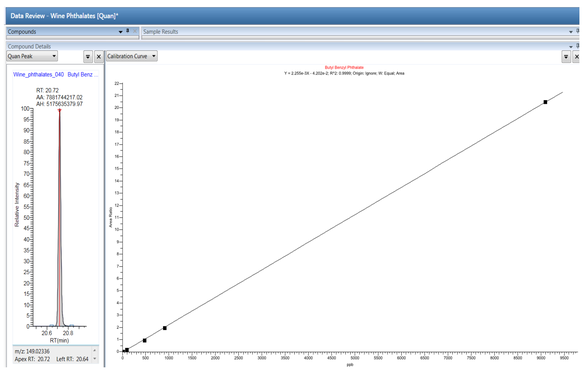
Q Exactive GC Mass Spectrometer Parameters	
Transfer line (°C):	260
Ionization type:	EI
Ion source(°C):	280 (EI)
Electron energy (eV):	70
Acquisition Mode:	Full scan
Mass range (*m/z*):	50-750
Mass resolution (FWHM at *m/z* 200):	60k
Lockmasses (*m/z*):	207.03235 281.05114 355.06993

Data was acquired and processed using the Thermo Scientific™ TraceFinder™ software. This single software package integrates instrument control, method development functionality, along with qualitative-screening and quantitation-focused workflows.

Results

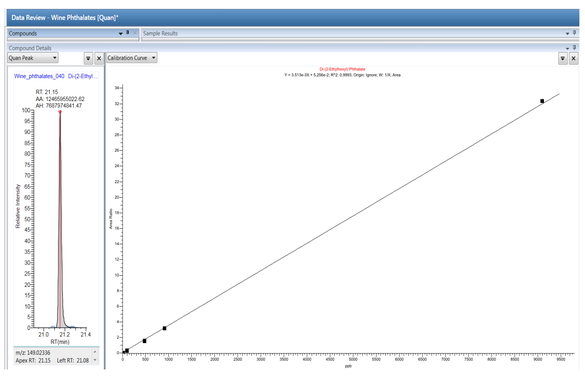
The Q Exactive GC system was operated in EI full scan mode using 60,000 (FWHM m/z 200) resolving power.
The Figure 1 shows the calibration curve form 1 to 10000 ng/mL in wine, with 3 replicates for each standard, of the extracted ion for BBP. The obtained R^2 is higher than 0.9999, showing excellent linearity over 4 orders.

Fig 2. Calibration curve for BBP. Each standard is injected 3 times.



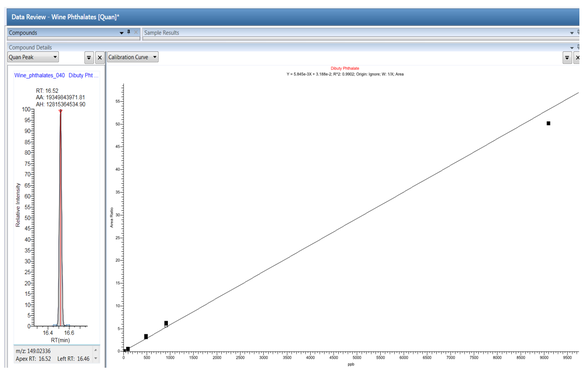
The Figure 3 shows calibration curve form 1 to 10000 ng/mL in wine, with 3 replicates for each standard, of the extracted ion for DEHP. The obtained R^2 is as well very good, being higher than 0.9993.

Fig 3. Calibration curve for DEHP. Each standard is injected 3 times



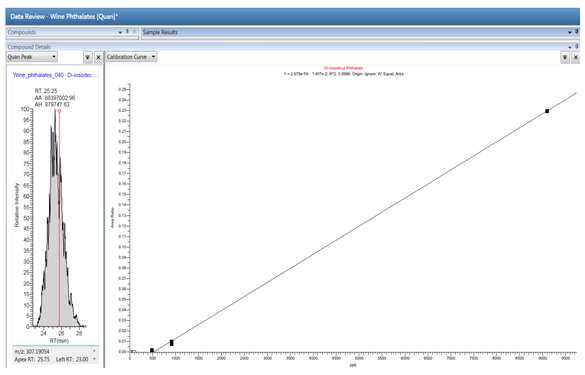
The Figure 4 shows calibration curve form 1 to 10000 ng/mL in wine, with 3 replicates for each standard, of the extracted ion for DBP. The obtained R^2 is higher than 0.9902.

Fig 4. Calibration curve for DBP. Each standard is injected 3 times.



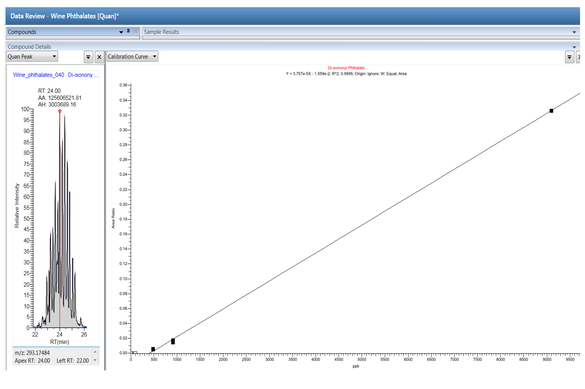
The Figure 5 shows calibration curve form 1 to 10000 ng/mL in wine, with 3 replicates for each standard, of the extracted ion for DIDP, the obtained R^2 is higher than 0.9996.

Figure 5 Calibration curve for DIDP. Each standard is injected 3 times.



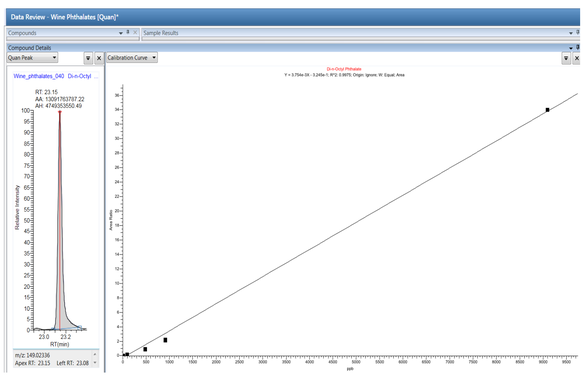
The Figure 6 shows calibration curve from 1 to 10000 ng/mL in wine, with 3 replicates for each standard, of the extracted ion for DINP. The obtained R^2 is higher than 0.9995.

Figure 6 Calibration curve for DINP. Each standard is injected 3 times.



The Figure 7 shows calibration curve from 1 to 10000 ng/mL in wine, with 3 replicates for each standard, of the extracted ion for DNOP. The obtained R^2 is higher than 0.9975.

Figure 7 Calibration curve for DNOP. Each standard is injected 3 times.



CONCLUSIONS

The results of this evaluation demonstrate that the Thermo Scientific Q Exactive GC hybrid quadrupole- Orbitrap mass spectrometer, in combination with TraceFinder software, is an extremely effective tool for the routine analysis of phthalates in wine samples.

The Orbitrap mass spectrometer delivers excellent resolving power, mass accuracy, and sensitivity.

It is vital to avoid cross contamination and reduce the blanc level, we recommend the use of Total Recovery Vials and Foil Closures, as well as quality glasses for the sample preparation.

ACKNOWLEDGMENT

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TRADEMARKS/LICENSING