IDENTIFYING NON-INTENTIONALLY ADDED SUBSTANCES (NIAS) IN FOOD CONTACT MATERIALS

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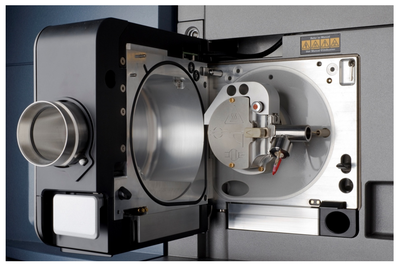
INTRODUCTION

Concern about the safety of food products has increased dramatically with intentionally and non-intentionally added substances (NIAS) used in packaging being of particular interest.

Screening analysis is required to identify chemicals that are present in the packaging. This step usually involves an organic solvent extraction and injection via GC coupled to a quadrupole MS equipped with electron ionization (EI) for volatiles/semi-volatiles as 70 eV scientific libraries are commonly available. However, the identification process requires extensive manual interpretation along with prior technical knowledge when the compound is not listed in the library.

Atmospheric Pressure Gas Chromatography (APGC) is a soft ionization technique enabling the generation of the molecular ion. High resolution MS together with the simultaneous MS^E acquisition of molecular and fragment ions generates accurate mass measurements and isotopic pattern and sub-structure information that are all useful in determining elemental composition. APGC and high resolution MS together with a workflow driven process was used to identify unknown compounds in packaging.



METHODS

Sample Preparation

The sample, consisting of novel starch-based biopolymer pellets (0.5 g), was extracted three times with 2.5 mL of methanol in an ultrasonic bath for 1 hour at 40 °C. The combined extraction solution was concentrated to 1.0 mL under a gentle nitrogen flow at room temperature.

GC Conditions

GC system:	Agilent 7890A
Autosampler:	7683B
Column:	DB-5MS, 30 m x 0.25 mm x 0.25 µm
Injection:	1 µL pulsed splitless, 1.2 min, 32 psi
Inlet temperature:	250 °C
Carrier gas:	Helium @ 1 mL/min
Oven temperature:	50 °C (2 min) → 300 °C @ 10 °C/min (10 min)

APGC-MS Conditions

MS system:	Xevo G2-XS QTof
Ionization:	APGC
Analyser:	Sensitivity mode
Corona current:	2.2 µA
Source temperature:	150 °C
Sampling cone:	30 V
Mass range:	*m/z* 50 – 650
Cone gas flow:	140 L/h
Auxillary gas flow:	225 L/h
Make-up gas:	Nitrogen @ 300 mL/min
Lock mass:	GC column bleed (*m/z* 207.0324)
Collision energy:	20 - 30 eV for MS^E

APGC data were acquired using dry conditions, where nitrogen charge transfer mainly occurs and gives rise to the (radical cation) molecular ion, $M^{+\cdot}$. Even under dry conditions some structures give rise to the protonated molecular ion, $[M+H]^+$ because moisture cannot be completely eliminated from the source. Significant components were located using binary comparison to an extracted solvent blank.

Data Management

Data were acquired, processed and reviewed using UNIFI Scientific Information System v1.8.2.

RESULTS AND DISCUSSION

APGC compared to EI

Chromatograms acquired with EI (Agilent 6890N GC, 5975B detector) and APGC were compared, with the number of peaks detected by APGC being far higher (Figure 1). This is due to the higher sensitivity of Q/Tof versus single quadrupole, and to the intrinsic characteristics of the two different ionization techniques.

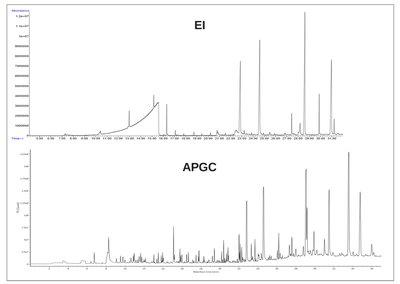


Figure 1. Comparison of Total Ion Chromatograms from EI and APGC.

One component at 16.3 min delivered a high *match* factor of 917 from a NIST 14 library search of EI spectra and was identified as 1,6-Dioxacyclododecane-7,12-dione. The same component in APGC showed a base peak at *m/z* 201.1120, attributed to the $[M+H]^+$ ion. APGC is a 'soft' ionization technique which results in lower fragmentation (Figure 2). The presence of abundant molecular ions highlighted the usefulness of APGC coupled with high resolution MS when detection and confirmation of the molecular formula is required.

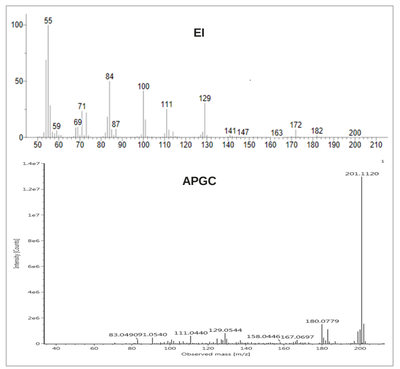


Figure 2. Comparison of spectra from EI and APGC.

Correcting tentative identifications

A second component at 17.2 min delivered a lower *match* factor of 787 that NIST attributes to 3,4-Altrosan or beta-D-Glucopyranose, 1,6-anhydro-. Both have a molecular weight of 162 amu. A base peak at *m/z* 232.1817 appears when analysing the same peak in APGC. The data was acquired in MS^E mode so componentised low and high collision energy spectra allowed the spectra to be cleaned up (Figure 3).

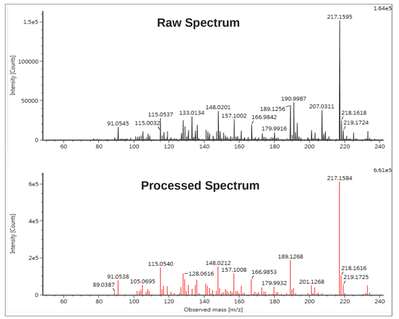


Figure 3. High collision energy spectra before and after processing.

The clean spectrum was submitted to an elucidation process for identification, including searching online databases for tentative structures. Accurate masses of the precursor ion and fragment ions helped to attribute the candidate structure to 1,2,3,4-Tetrahydro-1-methoxy-1,6-dimethyl-4-(1-methylethyl) naphthalene (Figure 4). This highlighted the combination of APGC and the structural elucidation workflow to correct EI identifications that present a low *match* value.

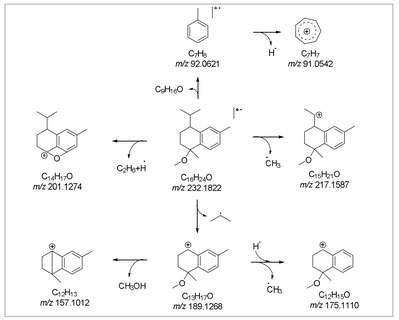


Figure 4. Proposed fragmentation pathway for candidate.

Identifying previously undetected peaks

A third component at 27.3 min illustrated how APGC can extend the identification process to a wider range of compounds that were not always detected in EI (Figure 5).

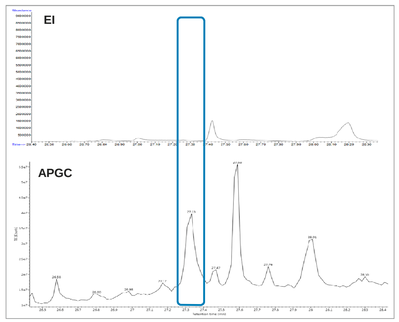


Figure 5. Comparison of chromatograms in the range 26.4-28.4 min.

Here the structural elucidation workflow was employed on the base peak at *m/z* 410.3169. UNIFI attributes a number of different candidates following an automatic search in Chemspider. The table shows a list of possible compounds sorted by Predicted Intensity, i-FIT Confidence, Fragment Match or number of citations (Figure 6).

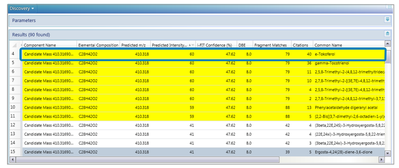


Figure 6. Results from the Discovery tool in UNIFI for the component at m/z 410.3169 and 27.33 min.

After elucidating the most important fragment ions by applying common organic chemistry rules, and checking their molecular formulae, the unknown compound was identified as e-Tokoferol, more commonly called beta-tocotrienol (Figure 7). This highlighted the combination of APGC and the structural elucidation workflow in UNIFI to provide broader coverage for NIAS compounds.

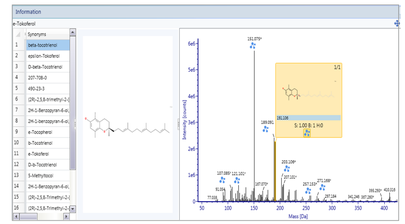


Figure 7. Discovery tool output of beta-tocotrienol with one of the major fragments (m/z 191.1062) highlighted.

CONCLUSION

- **Identifying unknown compounds in Food Contact Materials is usually a challenging process.**
- **UNIFI Software processes and aligns data containing accurate mass precursor and fragment ion information acquired by the MS^E functionality.**
- **EI-MS and APGC-Q/Tof systems have been proven to be complementary when the compounds of interest are described in commercially available libraries.**
- **APGC-Q/Tof is particularly advantageous when the elucidation is required for volatile and semi-volatile components not listed in the libraries or for those at trace or ultra-trace levels.**
- **APGC-Xevo G2-XS QTof and UNIFI together can challenge possible erroneous identifications and also facilitate the component identification for peaks that are not detected using an EI-single quadrupole MS.**
- **Finally, UNIFI componentization reduces the burden of data interpretation for the analyst, decreases potential false-positive assignments, and allows results to be presented clearly and concisely.**

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