Fully Automated QuEChERS for Organochlorine and Organophosphate Pesticides in Tomato Juice and Red Wine

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Overview

Using PAL Robotic Tool Change (RTC) system, a fully automated QuEChERS was developed for the extraction and clean-up of organochlorine and organophosphate pesticides from homogeneous samples. The automated QuEChERS workflow includes extraction with acetonitrile, salting out with saturated sodium chloride solution and the clean-up with PAL µSPE prior to injection into the GC-MS/MS for analysis. Method validations were achieved by using the automated matrix matches calibration spiked from 1 ng/mL to 100 ng/mL of organochlorine and organophosphate pesticide standards into the PAL µSPE-cleaned tomato juice and red wine samples. The matrix match calibration curve linearities were at R^2 0.995 or better. By spiking 10 ng/mL of pesticide standards into a raw tomato juice and red wine, the recoveries were obtained in the range of 70% - 130%, with n = 6 samples to determine the automated workflow precisions.

Introduction

QuEChERS is the quick, easy, cheap effective, rugged and safe sample preparation method developed by M. Anastassiades and S.J. Lehotay in 2003. Since then, this technique has become the widely used sample preparation approach in pesticide residue analyses. According to the QuEChERS website, about 45 min are needed to manually prepare 8 samples in the laboratory [1]. In the QuEChERS method, acetonitrile is used as extraction solvent, followed by adding NaCl and buffer salts. After shaking and centrifugation traditionally dispersive solid phase extraction (dSPE) is used for extract clean-up before analysis by GC-MS or LC-MS. High matrix load in GC-MS, the matrix effects in LC-MS, enhancing or suppressing analyte signals, varying extraction recoveries were major challenges that were approached to overcome by many matrix specific modified clean-up agents and procedures.

Analytical Strategy

Using PAL µSPE in Matrix Clean-Up

A cartridge based miniaturized solid phase extraction, known as PAL µSPE, was fully automated by using the PAL RTC system to perform the fully automated QuEChERS preparation workflow.

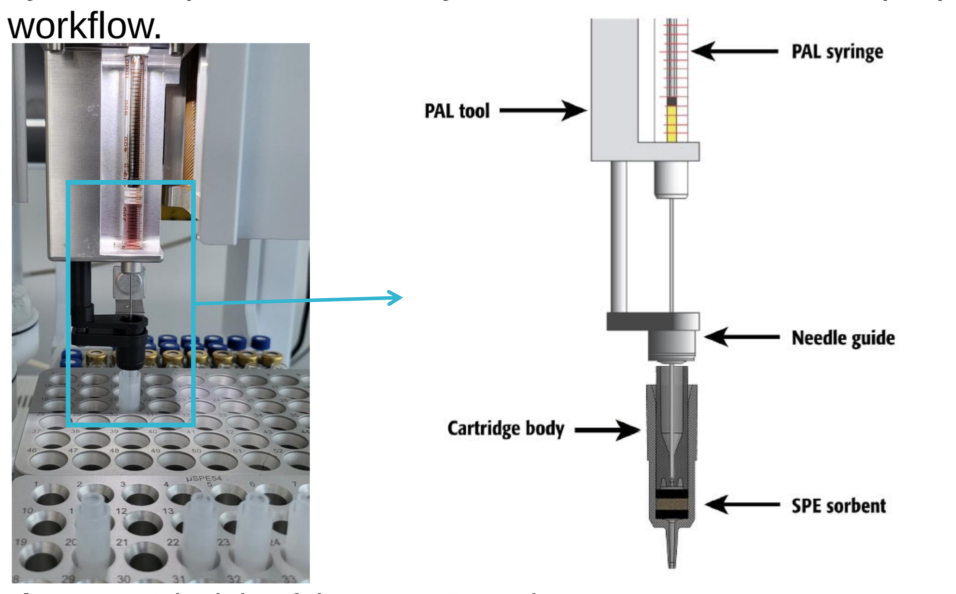

Figure 1. Principle of the PAL µSPE clean-up

An optimized sorbent bed for GC QuEChERS analysis, containing a mixture of 45 mg of $MgSO_4$, PSA, C18EC and CarbonX was filled by CTC Analytics into proprietary PAL µSPE cartridges. This PAL µSPE cartridges work in scavenging mode to retain the sample matrix inside the sorbent bed. A clean extract delivering the pesticide compounds is eluted into empty vials beneath the cartridges for online injection to GC-MS.

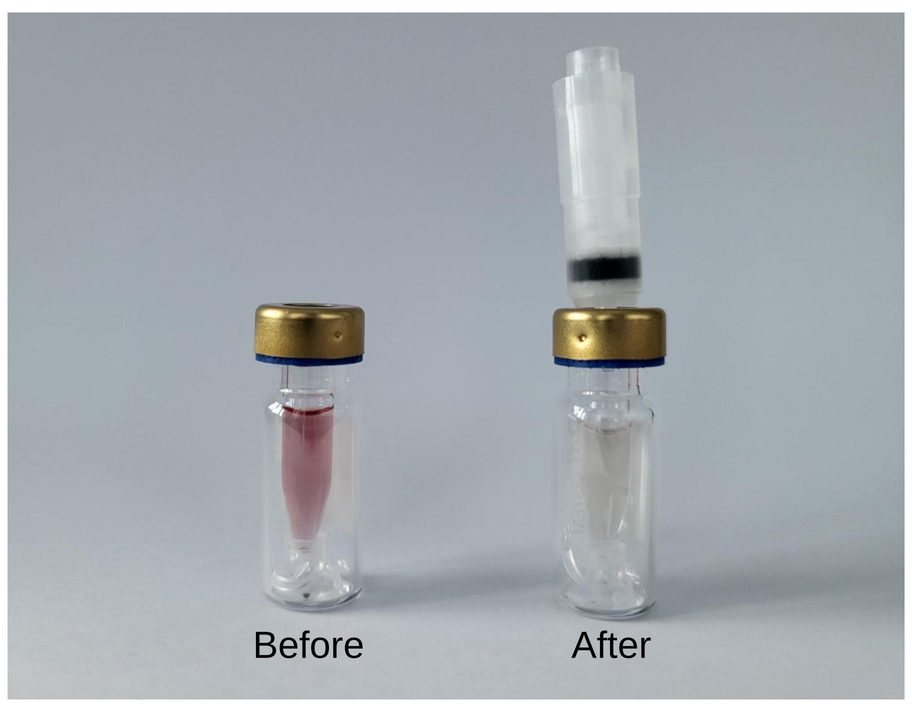

Figure 2. Red wine sample, before and after the PAL µSPE clean-up

Instrument Setup

The fully automated workflow, including sample blank, post spike with calibration and internal standards was carried out with the instrument setup as shown in **Figure 3**. The automated QuEChERS was established by the PAL RTC system with a vortexing module, solvent module to store up to 100 mL of acetonitrile and saturated sodium chloride solution, a fast wash module with acetonitrile and water for active syringe wash. In the Tray Holder, as shown in **Figure 3**, rack 1 was used to place the tomato juice and red wine samples in 2 mL vials. The clean up cartridges were placed on the dedicated cartridge holder in rack 3. Empty vials with slitted septa were placed at the center rack 2 underneath of the aluminium vial cover to receive cleaned extract.

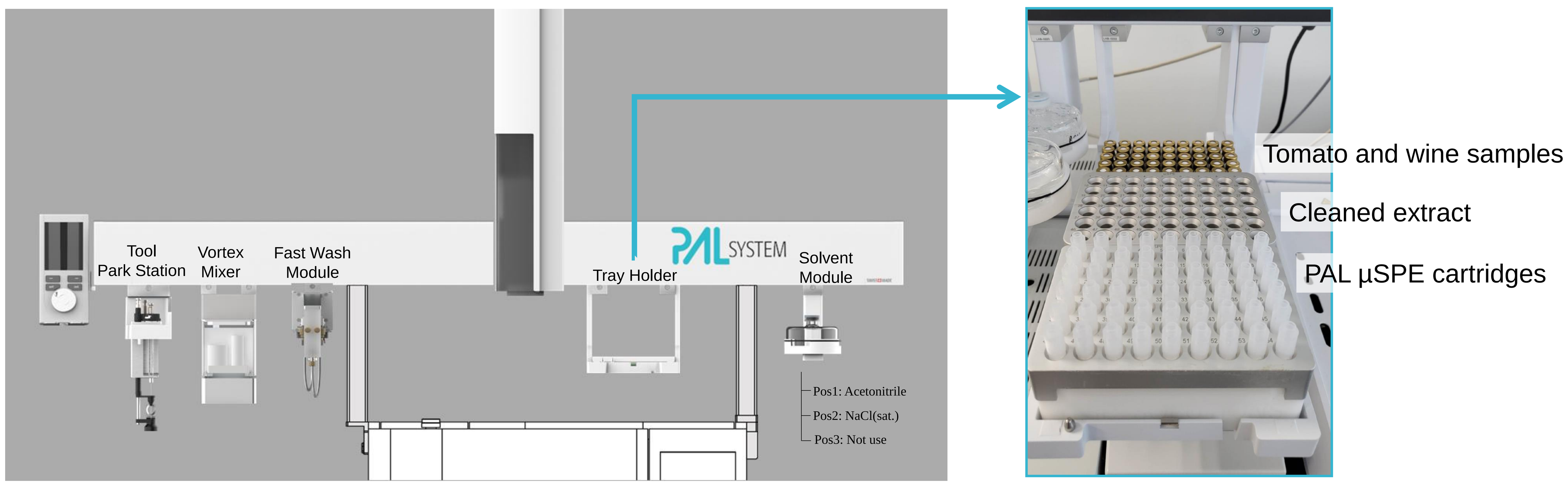

Figure 3. PAL RTC system configuration for the fully automated QuEChERS analysis

Automated QuEChERS Workflow in Analyzing Tomato Juice and Wine Samples

The only manual step in the automated QuEChERS workflow was a pipetting of 500 µL of sample into 2 mL autosampler vials. The subsequent steps such as adding Acetonitrile, salt solution and clean-up by PAL µSPE were carried out automatically by the PAL RTC system based on the workflow shown in **Figure 4**. The organic and aqueous phases were well separated after adding in the saturated salt solution. No centrifugation was required. The PAL µSPE cartridge with $MgSO_4$, PSA, C18EC and CarbonX sorbents provided a high clean-up efficiency, as shown in **Figure 5** for tomato juice and **Figure 6** for red wine samples.

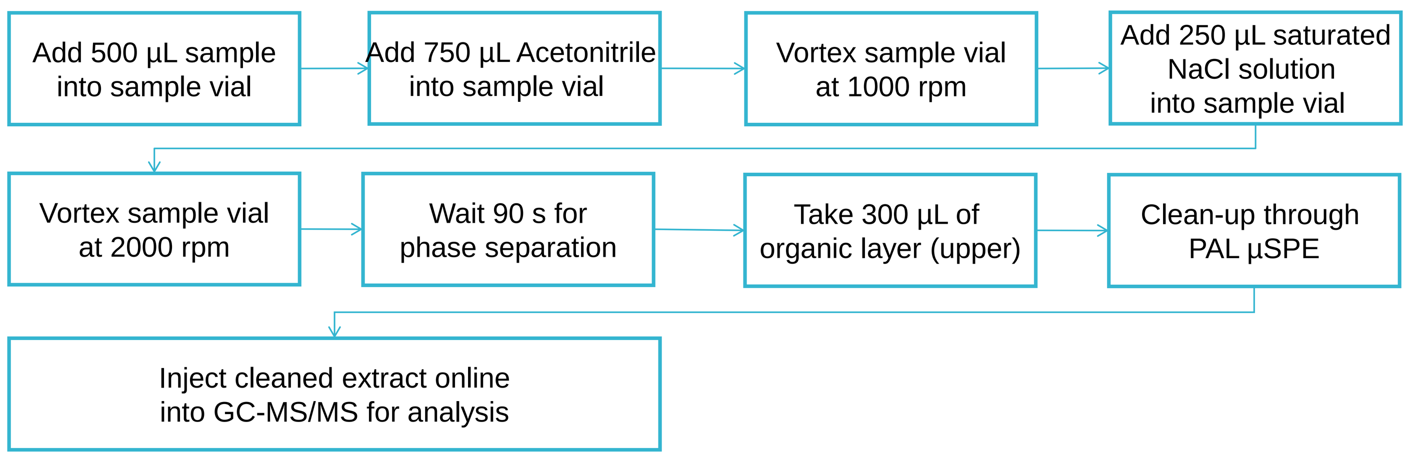

Figure 4. Automated QuEChERS workflow by PAL RTC System

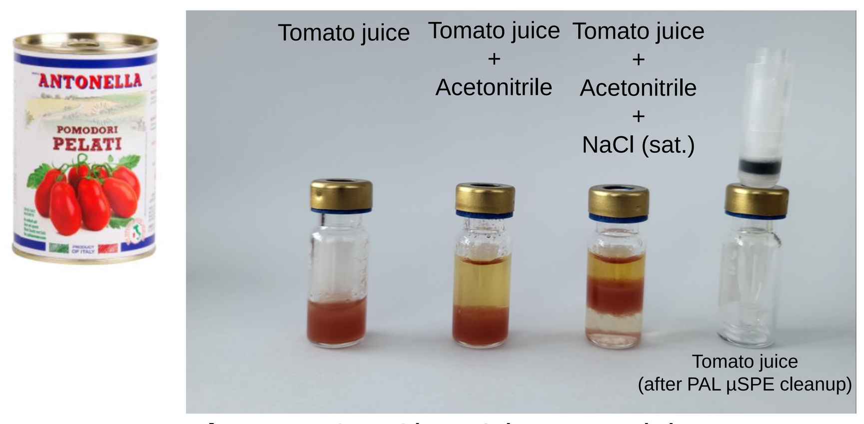

Figure 5. QuEChERS in tomato juice

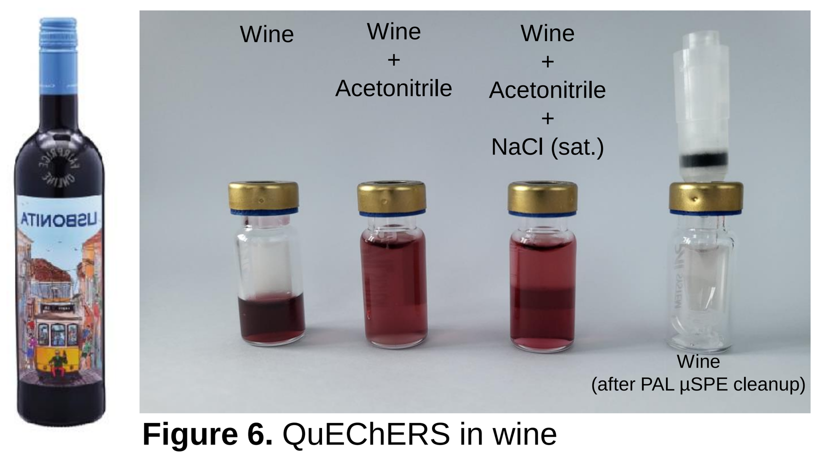

Figure 6. QuEChERS in wine

Results

Prior to analyzing the tomato juice and red wine samples, a Shimadzu GCMS-TQ8040, equipped with Rxi-5Sil MS (30 m x 0.25 mm x 0.25 µm) capillary column was optimized to achieve the detection limit to at least 1 ng/mL. A full MRM total ion chromtogram (TIC) of the 100 ng/mL organochlorine and organophosphate standards is shown as **Figure 7**. Upon completed QuEChERS extraction and clean-up, the tomato juice and wine samples were injected at 3 µL into this optimized GC-MS/MS system for analysis.

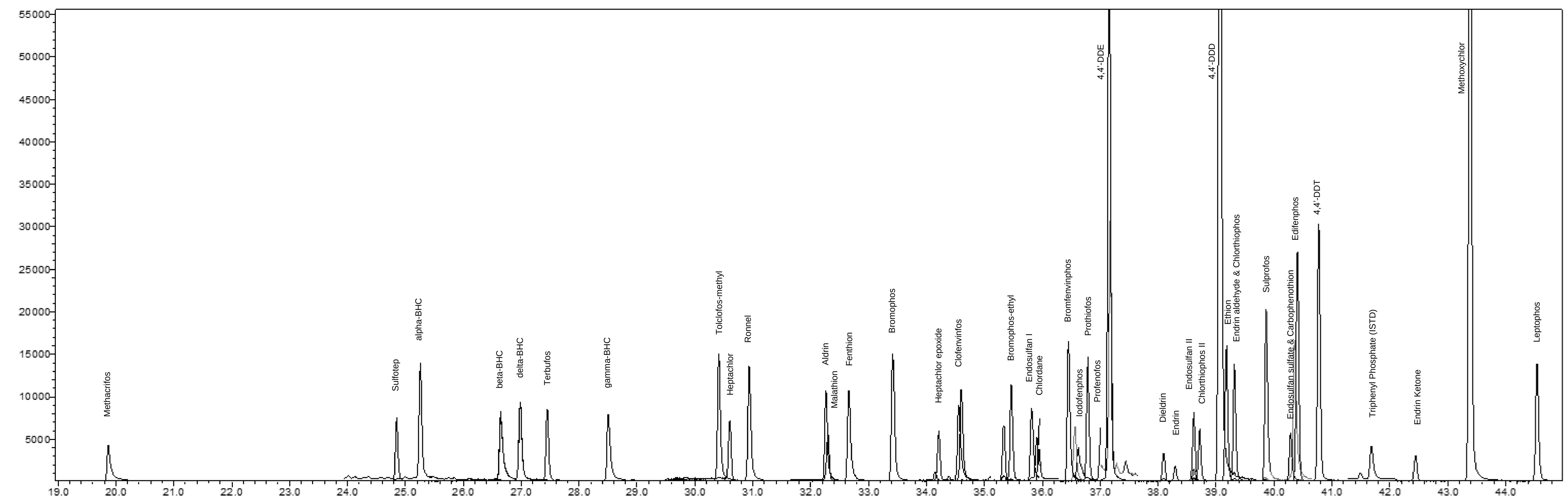

Figure 7. Total Ion Chromatograms (TICs) of 100ng/mL organochlorine and organophosphate pesticide standards by the GC-MS/MS.

Compounds (based on elution order)	Tomato Juice			Red Wine		
	Linearity	Precision %RSD (n=5)	Recovery	Linearity	Precision %RSD (n=6)	Recovery
Methacrifos	0.9995	8%	129%	0.9984	24%	103%
Sulfotep	0.9990	7%	94%	0.9982	16%	87%
alpha-BHC	0.9977	13%	104%	0.9924	20%	101%
beta-BHC	0.9956	6%	115%	0.9958	12%	115%
delta-BHC	0.9966	7%	118%	0.9956	11%	115%
Terbufos	0.9994	8%	108%	0.9953	14%	81%
gamma-BHC	0.9991	9%	87%	0.9979	13%	113%
Tolclofos-methyl	0.9998	5%	107%	0.9998	10%	114%
Heptachlor	0.9972	5%	99%	0.9969	20%	84%
Ronnel	0.9990	4%	105%	0.9970	10%	112%
Aldrin	0.9989	15%	85%	0.9973	21%	72%
Malathion	0.9972	9%	86%	0.9960	13%	115%
Fenthion	0.9964	10%	112%	0.9986	11%	106%
Bromophos	0.9990	8%	104%	0.9994	9%	109%
Heptachlor epoxide	0.9961	13%	84%	0.9973	13%	86%
Clofenvinfos	0.9608	12%	89%	0.9971	13%	111%
Bromophos-ethyl	0.9977	3%	86%	0.9995	8%	68%
Endosulfan I	0.9959	5%	79%	0.9997	16%	77%
tChlordane	0.9970	4%	115%	0.9985	17%	81%
Bromfenvinphos	0.9761	13%	80%	0.9989	28%	103%
Iodofenphos	0.9966	18%	91%	0.9993	16%	82%
Prothiofos	0.9989	10%	79%	0.9998	14%	69%
4,4-DDE	0.9982	15%	83%	0.9997	19%	86%
Profenofos	0.9865	10%	86%	0.9995	11%	94%
Dieldrin	0.9965	6%	112%	0.9985	18%	75%
Endrin	0.9968	12%	84%	0.9993	14%	101%
Endosulfan II	0.9984	6%	94%	0.9981	14%	107%
Chlorthiophos III	0.9982	11%	76%	0.9988	9%	64%
4,4'-DDD	0.9988	6%	102%	0.9985	15%	88%
Ethion	0.9980	6%	111%	0.9993	14%	83%
Endrin aldehyde	0.9988	3%	55%	0.9712	30%	91%
Chlorthiophos	0.9956	11%	81%	0.9992	13%	61%
Sulprofos	0.9990	8%	94%	0.9990	17%	76%
Endosulfan sulfate	0.9986	6%	115%	0.9996	13%	109%
Carbophenothion	0.9963	6%	92%	0.9990	11%	74%
4,4-DDT	0.9987	2%	147%	0.9990	19%	94%
Endrin ketone	0.9962	12%	95%	0.9985	11%	83%
Methoxychlor	0.9966	15%	136%	0.9979	18%	99%
Leptophos	0.9953	19%	59%	0.9967	6%	57%

Table 1. Linearity, precision, and recovery of the organochlorine and organophosphate pesticides in tomato juice and wine based on the fully automated QuEChERS sample preparation workflow and GC-MS/MS analysis.

Sample Evaluation

The organochlorine and organophosphate pesticide recoveries were evaluated based on pre- and post-spike of pesticide standards into the tomato juice and red wine samples, respectively. Matrix match calibration curves were generated by using the PAL RTC System to spike seven different concentrations ranging from 1 ng/mL to 100 ng/mL automatically into the cleaned tomato juice and red wine samples (prepared by the automated QuEChERS).

A series of five to six samples, spiked with 10 ng/mL organochlorine and organophosphate pesticide standards, were processed the full automated QuEChERS workflow to determine the recovery and precision based on the matrix match calibration curve. The detailed results of matrix match calibration curve linearity, precision and recovery of this fully automated QuEChERS sample preparation of tomato juice and red wine are listed in **Table 1**.

Conclusion

A fully automated QuEChERS based on the PAL RTC system is stable and reliable in the analysis of organochlorine and organophosphate pesticides from tomato juice and red wine.

References

[1] QuEChERS Home Page https://www.quechers.com/index.php (accessed Sep 7, 2020)

For the full report please request from GLIM@CTC.CH.