QUANTIFICATION OF ADDITIVES IN A COMMERCIAL CMP SAMPLE USING HPLC WITH PHOTODIODE ARRAY AND MASS DETECTION

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Best Poster Award Participant

BACKGROUND

Chemical mechanical polishing (CMP) or planarization slurries are used in the semiconductor industry to create a specific surface on a silicon wafer in the construction of various electronics.[1] To maintain the quality of the slurry, many chemical additives are used.

The routine analysis of additives in a CMP slurry can be helpful in formulation or quality control. Using a 15-minute separation method, the Waters Arc™ high performance liquid chromatography (HPLC) system with photodiode array (PDA) and ACQUITY QDa™ mass detection (MS) can be used for analysis of a CMP slurry and for individual additives or mixtures of additives in a quantitative analysis for those easily detected by PDA, and a qualitative analysis for those more challenging additives that require mass detection. The single quadrupole mass detector adds a second layer of detection that gives confidence in the results assay by providing a mass-to-charge (m/z) ratio unique to each molecule.

BENEFITS:
- Arc™ HPLC system with a routine 15-minute separation method and capable of in-system method update to UHPLC without re-validation.
- Robust XBridge™ BEH™ columns capable of low and high-pressure applications without compromising the column bed.
- ACQUITY™ QDa™ mass detector provided for more confidence in results assay.
- Empower™ 3 Chromatography Data System (CDS) for data analysis of PDA, QDa, and all Waters Arc HPLC compatible detectors.

THEORY/PURPOSE

Maintaining the quality of the CMP slurry during the polishing process is achieved by adding a fine balance of chemical additives that prevent slurry degradation due to friction, heat, oxidation, and evaporation. Examples of common CMP additives are polymers, complex organic molecules, organic acids, and mineral acids. Polymers are used as dispersing stabilizers. Complex organic molecules are used as corrosion inhibitors and biocides. Acids are used as chelating agents and pH adjusters.

Analytical methods are needed to ensure the quality of a CMP slurry, and most methods require complicated sample preparation and multiple instrument techniques to achieve results: gas chromatography-mass spectrometry (GC/MS), freeze drying, nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared (FTIR). ARC™ HPLC system with PDA detector and Waters ACQUITY QDa detector is a simple and routine analysis option. This instrument configuration is applied to a routine method for the analysis of known CMP slurry additives with minimal sample preparation. Additives are diluted for instrument injections, and the CMP slurry is centrifuged and diluted for instrument injections. The QDa single quadrupole mass detection confirms the additive qualitatively regardless of detection in the PDA, while the PDA detection enables quantitation for ultraviolet-active (UV) analytes at low concentrations.

OBJECTIVE

The goal of this work is to provide a routine analysis for additives in a CMP slurry that can be helpful for formulation or quality control. Using a 15-minute separation method, with the HPLC, PDA, and QDa configuration, the mass detection analysis of a CMP slurry, individual additives, or mixtures of additives is achieved. The detection of slurry chemicals is a quantitative analysis for those analytes easily detected by PDA, and a qualitative analysis for those more challenging additives that require mass detection. The single quadrupole mass detector adds a second layer of confidence in the results assay by providing a mass-to-charge ratio unique to each molecule.

Figure 1. Arc HPLC system, XBridge BEH columns, and ACQUITY QDa mass detector .

EXPERIMENTAL

SAMPLE DESCRIPTION:

Commercially available samples and standards were purchased (Merck, Germany) and are shown in Table 1. Each of these chemicals were chosen based on researching prior CMP analysis work.[2] The CMP slurry sample information was found on the Chempoint website along with the technical data sheet.[3] The benzotriazole, polyethylene glycol (PEG), citric and phosphoric acid were identified as common CMP slurry additives in a publication by Toray Research Center.[4] All the chemicals purchased, except for the CMP slurry, were dissolved in 10mM ammonium formate at a concentration of 1 mg/mL. The CMP slurry was centrifuged at a temperature of 4 ℃ at 2200 rpm for 20 minutes and the top 4 mL of supernatant were decanted into a 20 mL scintillation vial. The supernatant was diluted to a concentration of 6.5 mg/mL with 10 mM ammonium formate. Samples were made to an optimized concentration for injection onto the instrument.

Table 1. Chemicals used in the experiment.

Item #	Description	Slurry additive purpose	Molecule	Mwt
420778-1L	Ludox® TM-50 colloidal silica	Commercial CMP slurry	NA	NA
76457-50MG	Benzotriazole	Corrosion inhibitor		119.127
251275-100G	Citric acid ACS reagent	Chelating agent		192.123
WAT035711	PEG-27K	Dispersant		44.05 + 18.02
49865-500ML	Phosphoric acid	pH adjustment		97.994

EXPERIMENTAL (Cont.)

The Individual standards, at varying concentrations stated in Table 2, were serial diluted for individual calibration curves, were then combined one-to-one forming a CMP additive mixture (Mix A), and Mix A was serial diluted for a calibration curve. Finally, Mix A was diluted with the Ludox™ supernatant to form a Mix B dilution series for calculating the recovery of the additives spiked into the Ludox supernatant matrix. An example of PDA chromatography of CMP standard Mix A chromatography versus spiked Ludox CMP supernatant Mix B are compared in Figure 2.
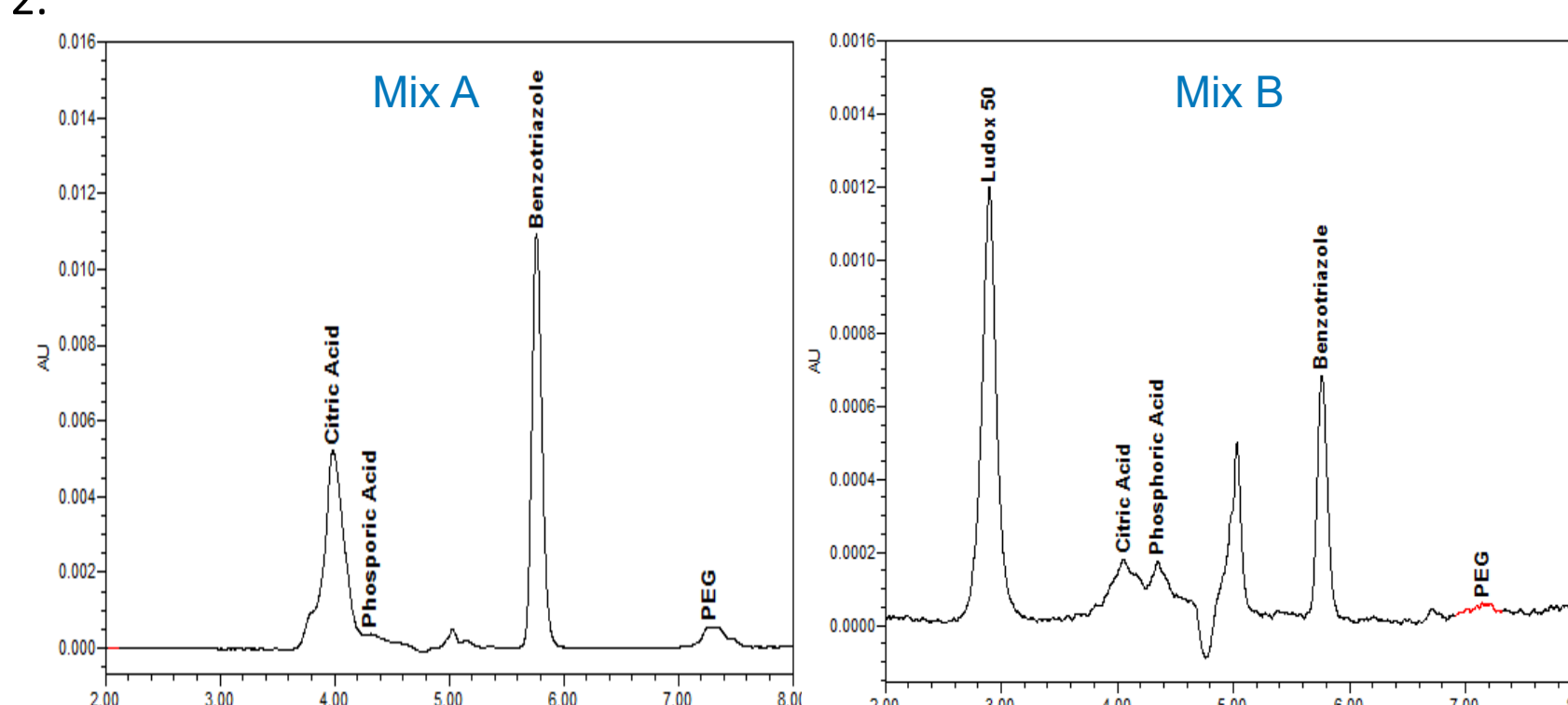

Figure 3. Example of PDA chromatography of Mix A (additive mix) vs. Mix B (spiked Ludox™ supernatant).

Additive Concentrations (Table 2)

Additive	Concentration (mg/mL)
Citric Acid	1
Benzotriazole	0.01
PEG	1
Phosphoric Acid	0.01

LC Conditions (Table 3)

Chromatographic System:	Arc™ HPLC
Pump:	Quaternary Solvent Manager
Sample Temperature:	20 ℃
Column Temperature:	50 ℃
PDA (wavelength)	254nm
Column set:	XBridge™ BEH™ 5 µm (2), (4.6 x 150mm)
Solvent A:	Water; Ammonium Formate 10mM
Solvent B:	Acetonitrile
Wash Solvent	80/20 Water/Acetonitrile
Seal Wash:	50/50 Water/Methanol
Flow Rate:	0.600 mL/min.
Injection Volume:	20 µL

Gradient Table (Table 4)

Time (min)	Flow (mL/min)	%A	%B	Curve
0	0.6	50	50	initial
0.5	0.6	50	50	6
3.0	0.6	5	95	6
4.0	0.6	5	95	6
5.0	0.6	50	50	6
6.0	0.6	50	50	6

MS Conditions (Table 5)

MS System:	Waters ACQUITY QDa™ Mass Detector
Ionization Mode:	ESI+/ESI-
Acquisition Range:	30-1200 Da
Cone Voltage:	15V
Data:	Centroid

RESULTS

The Ludox supernatant revealed one peak in the PDA while the QDa scan revealed multiple peaks. Some of these peaks were identified as common slurry additives by their m/z values in the CMP slurry supernatant as phosphoric acid, citric acid, polyethylene glycol (PEG), and L-proline (Figure 2).

For the QDa data, the CMP additive Mix A additives phosphoric (m/z 97), and benzotriazole (m/z 119) were extracted in positive ionization mode, and the citric acid (m/z 192) and PEG (m/z 44) additives were extracted in the negative ionization mode. The phosphoric acid and PEG were detected at low intensities with a small amount of background signal noise (Figure 3).
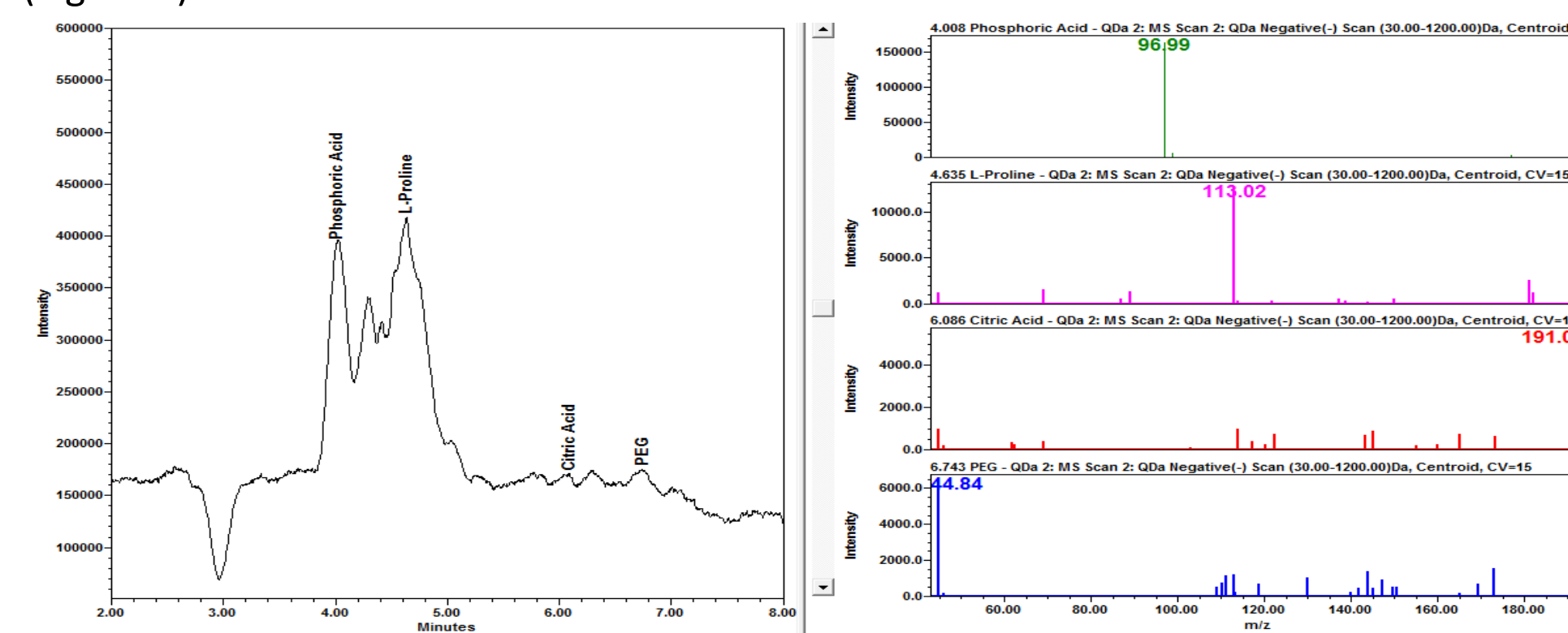

Figure 2. Negative QDa electrospray (ESI) mass spectra of Ludox supernatant confirms common CMP additives phosphoric acid, L-proline, citric acid and PEG molecular ions as $[M-H]^-$.

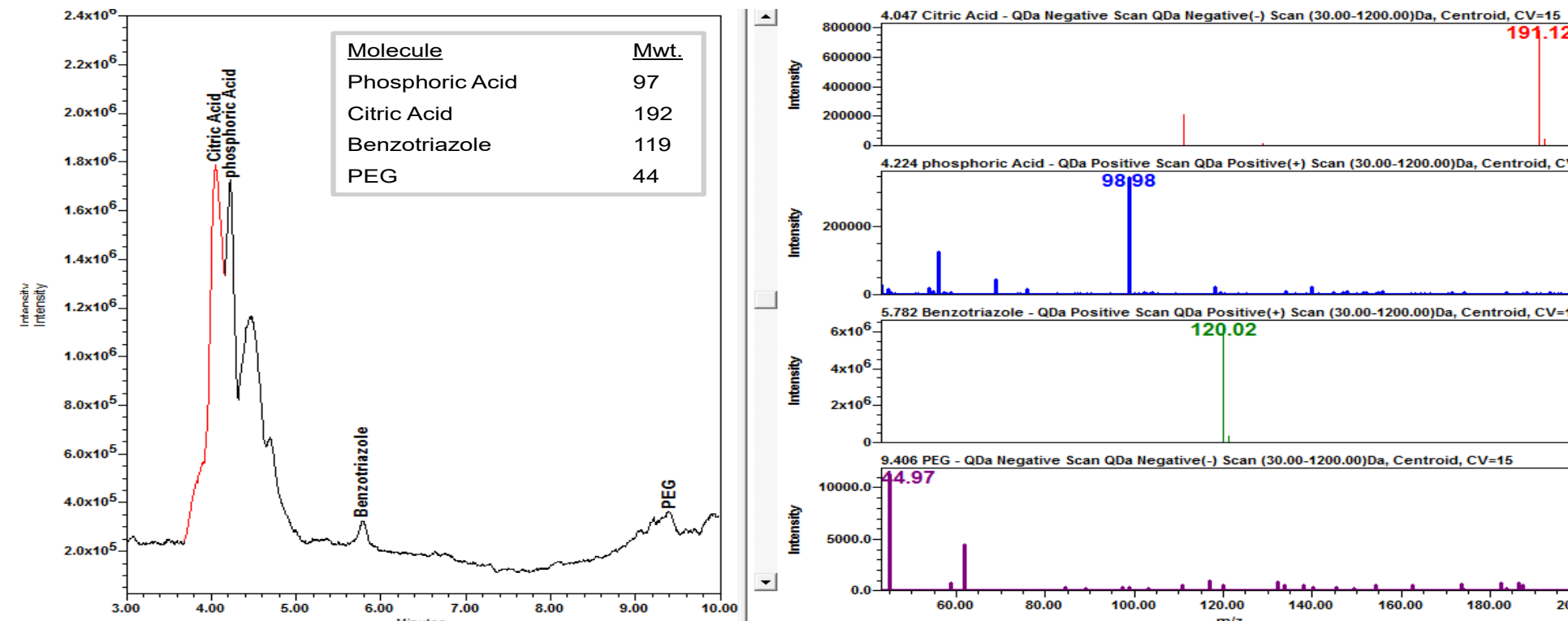| Molecule	Mwt
Phosphoric Acid	97
Citric Acid	192
Benzotriazole	119
PEG	44

Figures 3. Positive and negative QDa electrospray (ESI) mass spectra of the CMP standard additives Mix A with phosphoric acid and benzotriazole molecular ions confirmed as $[M+H]^+$ and citric acid and PEG as $[M-H]^-$.

The PDA data for 10 consecutive injections of additive Mix A was processed in Empower 3 software (Figure 4), and the data tables for peak retention time and peak area were reported (Tables 6a & 6b). The peak retention times had excellent %RSD < 0.1%. The peak areas had typical % RSD values expected in a mixture excluding the benzotriazole value. The higher area %RSD values are likely due to chemical interactions.

The PEG concentration in the mixture was optimized to overcome its low level of UV visibility and low intensity response in the QDa detector. The phosphoric acid in the additive mixture increased the PEG UV activity.[5] The benzotriazole was the most UV active chemical in the additive mixture due to its ring structure.

RESULTS (Cont.)

CMP Mix A: overlay of 10 consecutive injections.

Peak Retention Time

Additive	Mean	Std. Dev.	% RDS
Citric Acid	3.974	0.003	0.09
Benzotriazole	5.769	0.002	0.04
PEG	7.352	0.004	0.05

Peak Area

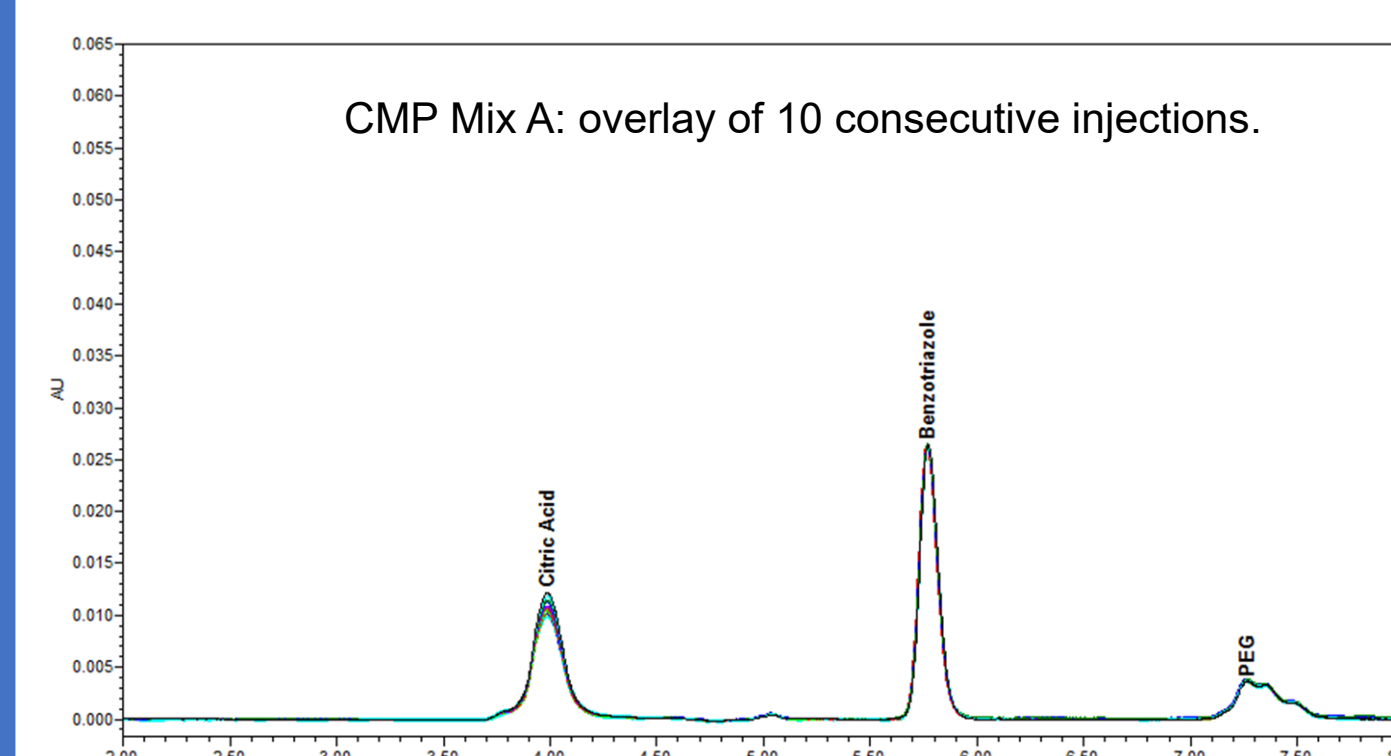| Additive	Mean	Std. Dev.	% RDS
Citric Acid	45242	4412	9.75
Benzotriazole	64385	169	0.26
PEG	5947	237	3.98

Figure 4 & Tables 6a and 6b. CMP additive Mix A overlay and Empower 3 System Suitability peak retention times and peak areas PDA data analysis.

To assess compound linearity calibration standards with concentrations ranging from 0.01 mg/mL to 1 mg/mL were prepared in solvent standards as well as in CMP slurry matrix and analyzed for each target compound. No internal standards were used.

The calibration response of the individual standards and the CMP Mix A are compared below, in figures 5a and 5b. Generally, the coefficient of determination R^2 was >0.995 indicating excellent linear response. There is a lower R^2 value (0.98) on the PEG curve in the additive mixture, and this change may be due to interaction of the PEG in the Mix A sample.
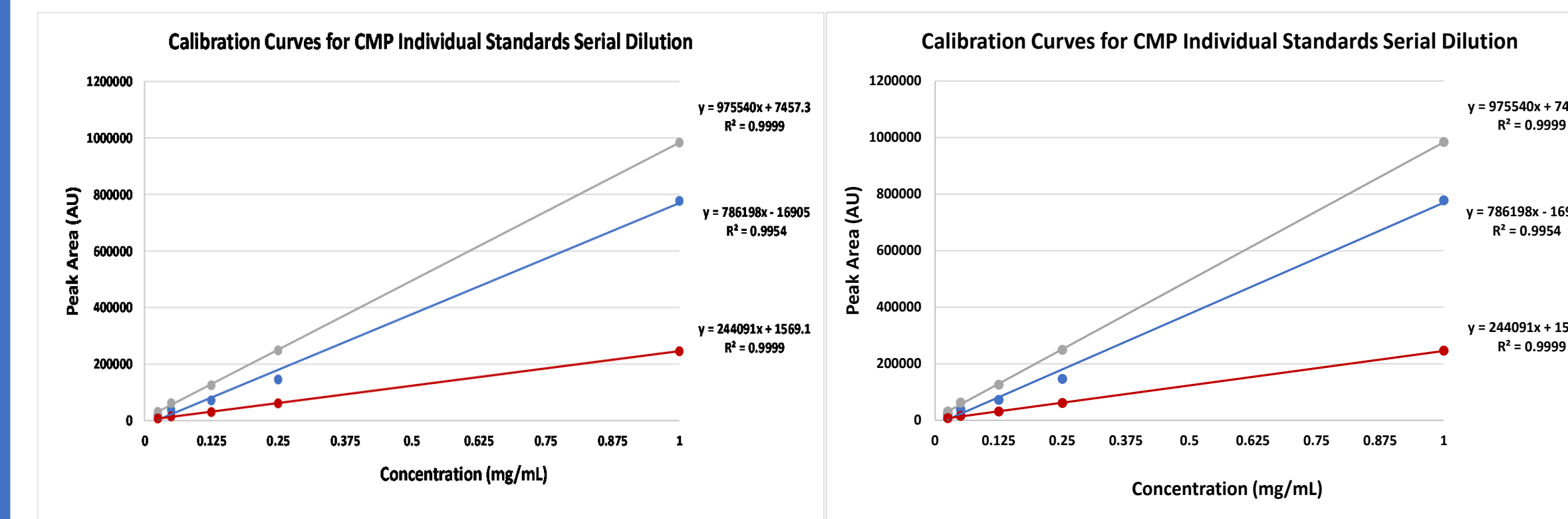

Figure 5a. Linearity of citric acid, benzotriazole and PEG assessed over a concentration ranging from 0.01- 1 mg/mL. One injection per calibration point was performed and no internal standard correction was applied.
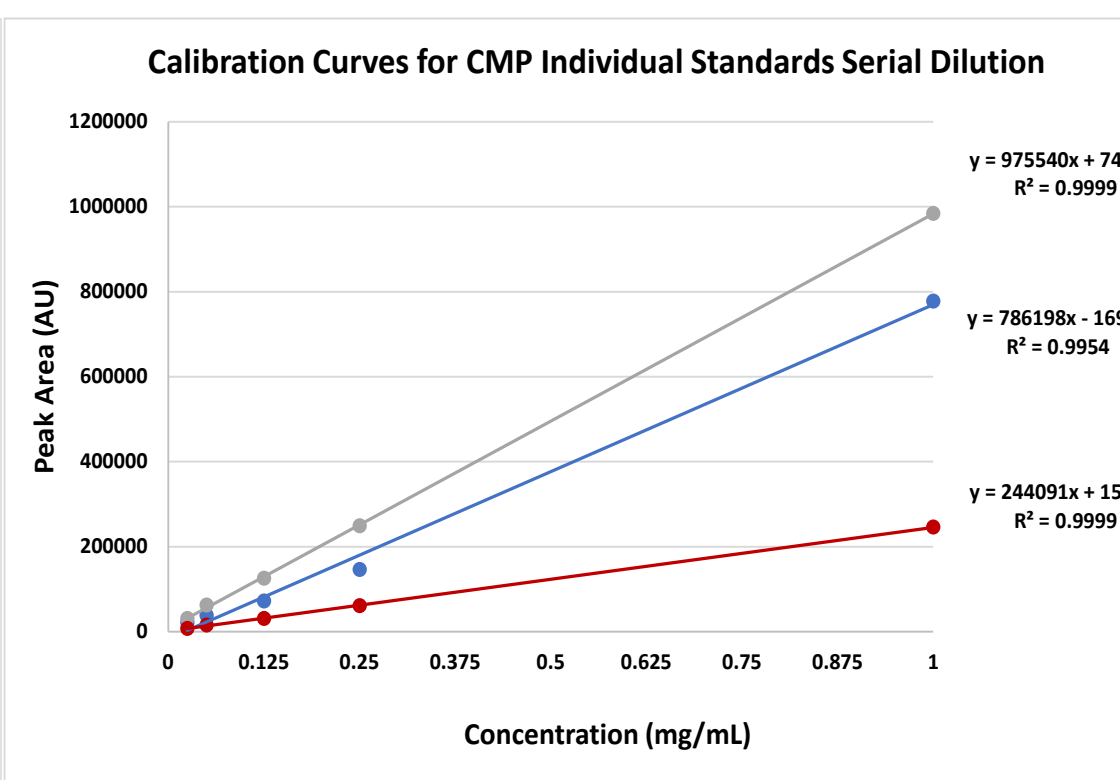
Figure 5b. Graph depicting PDA peak area data from the serial dilution of CMP Mix A.

The percent recovery of the CMP mixture individual standards spiked into the Ludox supernatant, based on PDA peak areas, is indicative of the limits of concentration detection within the method. The benzotriazole is recovered well with % recovery values between 99-101%, the citric acid is recovered at 78-83% that are likely due to a matrix effect, and the PEG is recovered at 81-111% (Figure 6).

The percent recovery of the CMP Mix A in a serial dilution using the Ludox® supernatant as a diluent was noted as having a large matrix effect. Benzotriazole was the only additive standard detected at all the dilution levels significant enough in the PDA for quantification use. Although the matrix effects were stronger in the citric acid and PEG in the Mix B, the citric acid did have some quantitative data as well as peaks from the QDa mass detector for qualitative data.
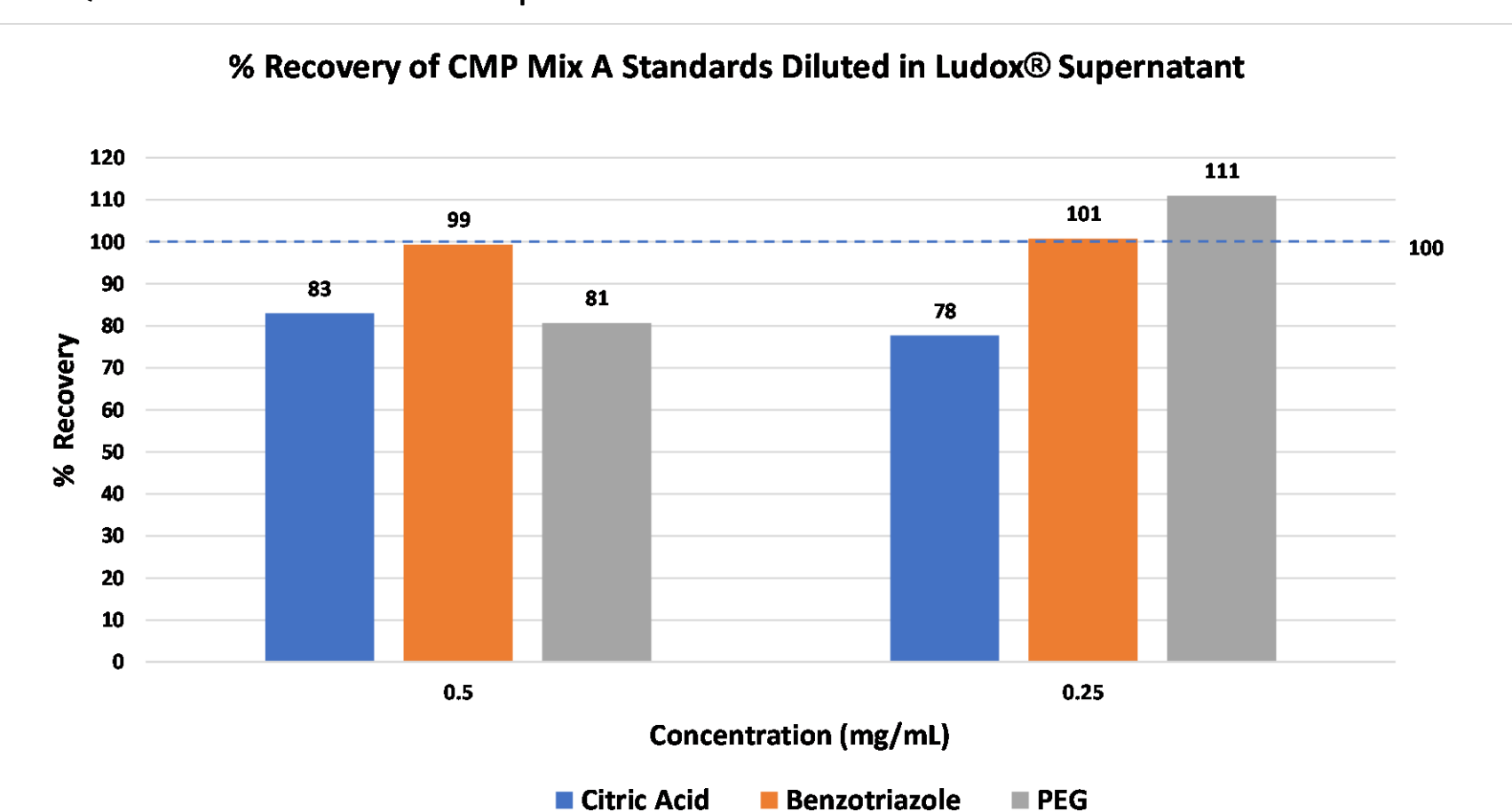

Figure 6. Graph depicting PDA peak area % recovery from Ludox supernatant spiked with CMP additive mixture.

CONCLUSION

- The results from the experiments performed demonstrate a simple, routine analytical approach for the analysis of additives in CMP slurry using Arc HPLC system coupled to PDA and single quadrupole mass detector.
- All target analytes were baseline separated on Waters XBridge BEH 5 µm column in under 15 minutes.
- Excellent repeatability of results was obtained as demonstrated by calculating peak area %RSD for citric acid, benzotriazole and PEG with %RSD values between 0.3-10% (n=10 consecutive injections).
- Retention time stability was achieved with %RSD <0.1%, and linearity of the calibration curves for the standards produced R^2 values at >0.995.
- Overall, the combination of Arc HPLC system with PDA and QDa mass detectors can be routinely used for robust and confident quantification of CMP slurries additives. Empower 3 CDS enables acquisition, processing and reporting of data acquired with the PDA and the QDa mass detectors in one software platform.

IMPACT OF THIS WORK/OUTLOOK

Great expectations!

References

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