

Pre-concentration and a Novel Scan Function for More Sensitive and Stable Ambient Ionization Mass Spectrometry

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ABSTRACT

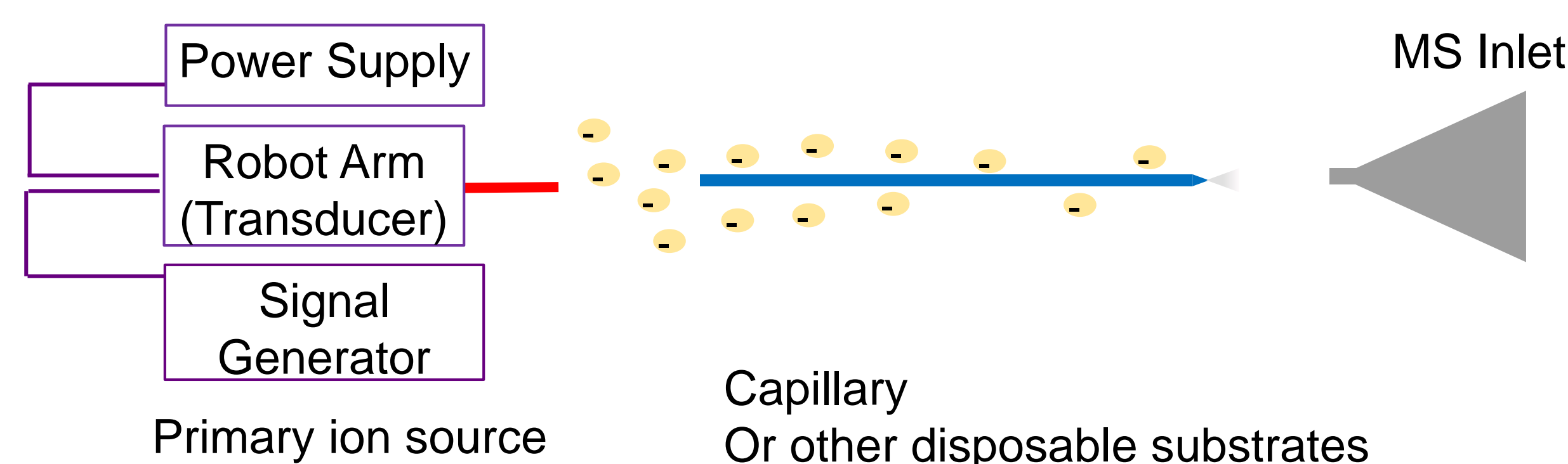
- Purpose:** To develop an all-in-one preconcentration ion source for rapid quantitative analysis of part-per-trillion environmental contaminants;
- Methods:** The pre-concentration method was coupled with contactless ionization technique, and new ion trap quantitative scan functions;
- Results:** 1) Pre-concentration: ppt level analytes preconcentrated to ppb levels readily offline; 2) Ambient ionization: piezoelectric inkjet delivered pico-liter solvent for analyte extraction, prior to contactless ESI ionization; 3) MS/MS scan: the precision of quantitative analysis improved when performing all MS/MS scan from the same ion injection event;

INTRODUCTION

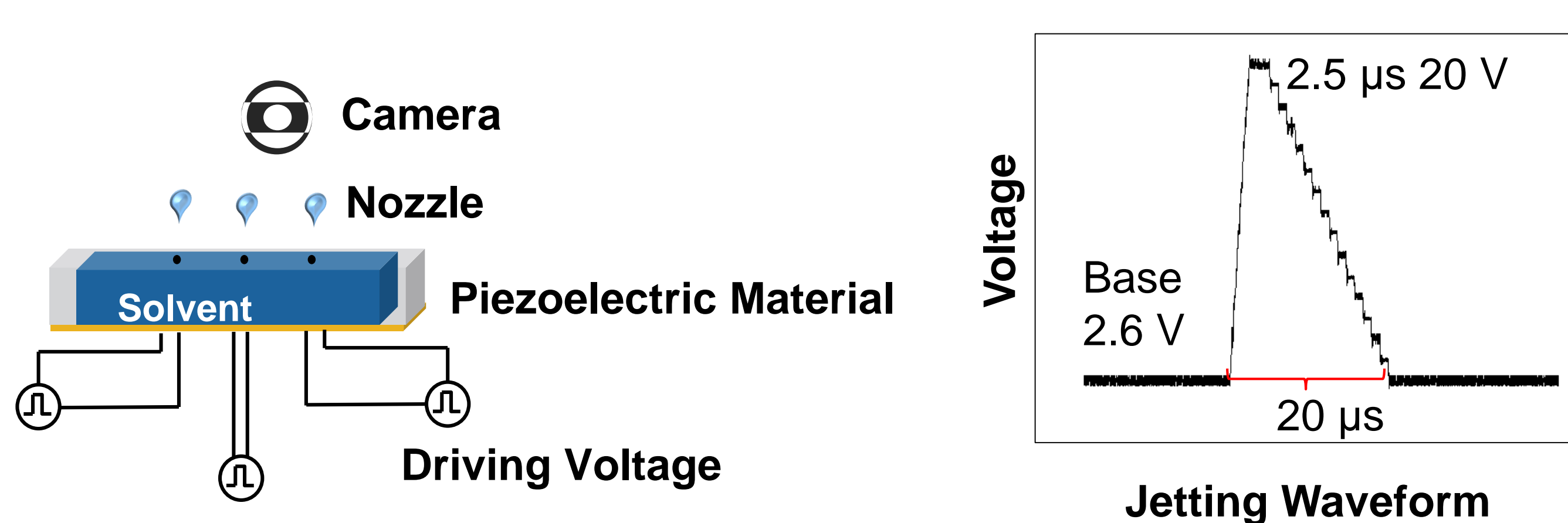
- Ambient mass spectrometry (AMS) is a group of ionization techniques operated at atmospheric pressure without tedious sample pretreatment. Albeit quick and simple, it is challenging to directly analyze parts-per-trillion level of compounds in environmental samples.
- In practical environmental analysis, various of contaminants, such as perfluorinated compounds, are well below the limit of detection (LOD).^[1]
- The development of a simple, universal, and robust pre-concentration technique will greatly facilitate the quantitative application of AMS.

METHODS

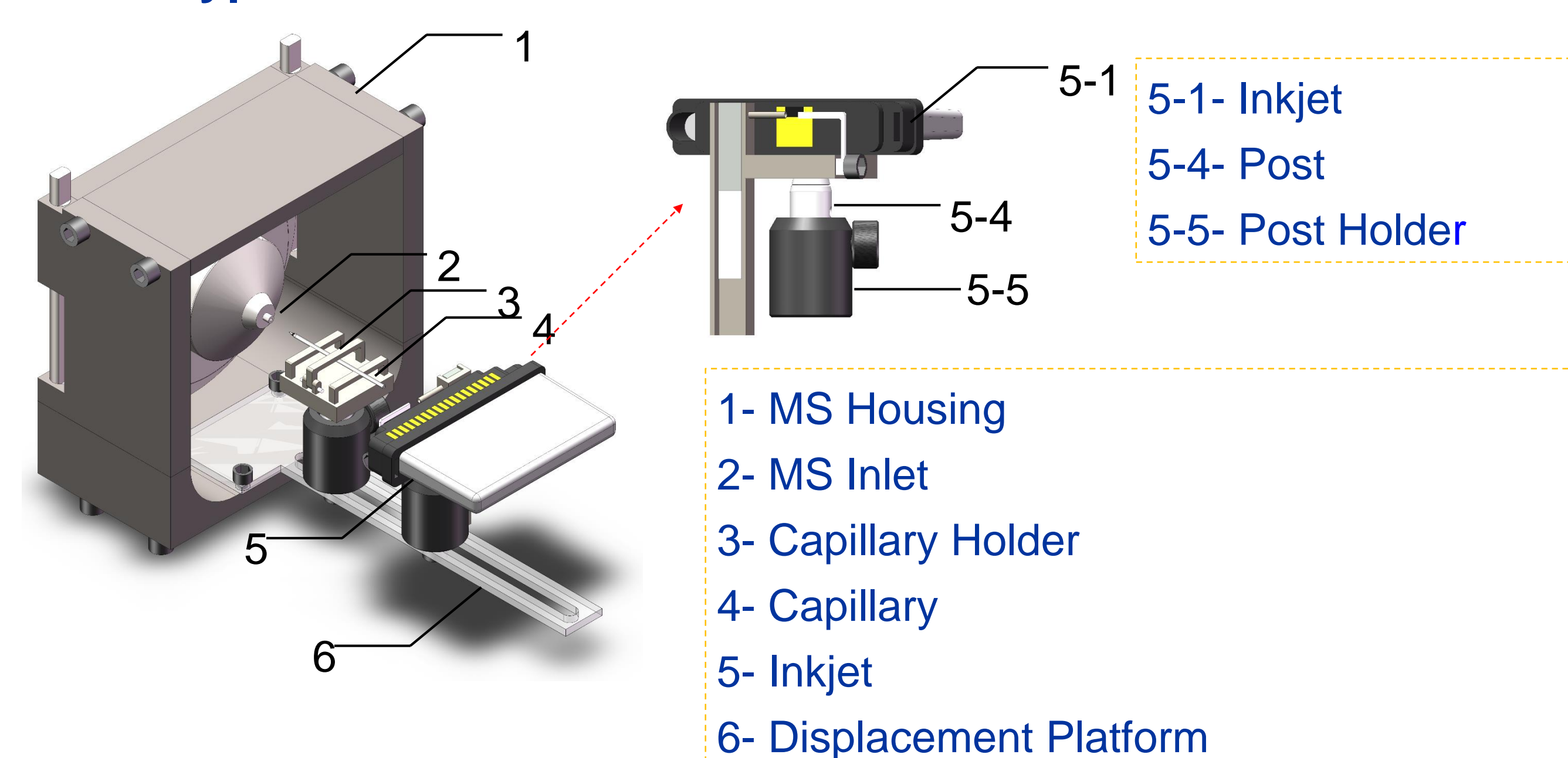
1. Schematic of Contactless Mechanical Relay ESI^[2]



2. Schematic of Piezo inkjet Printer and Driving Waveform

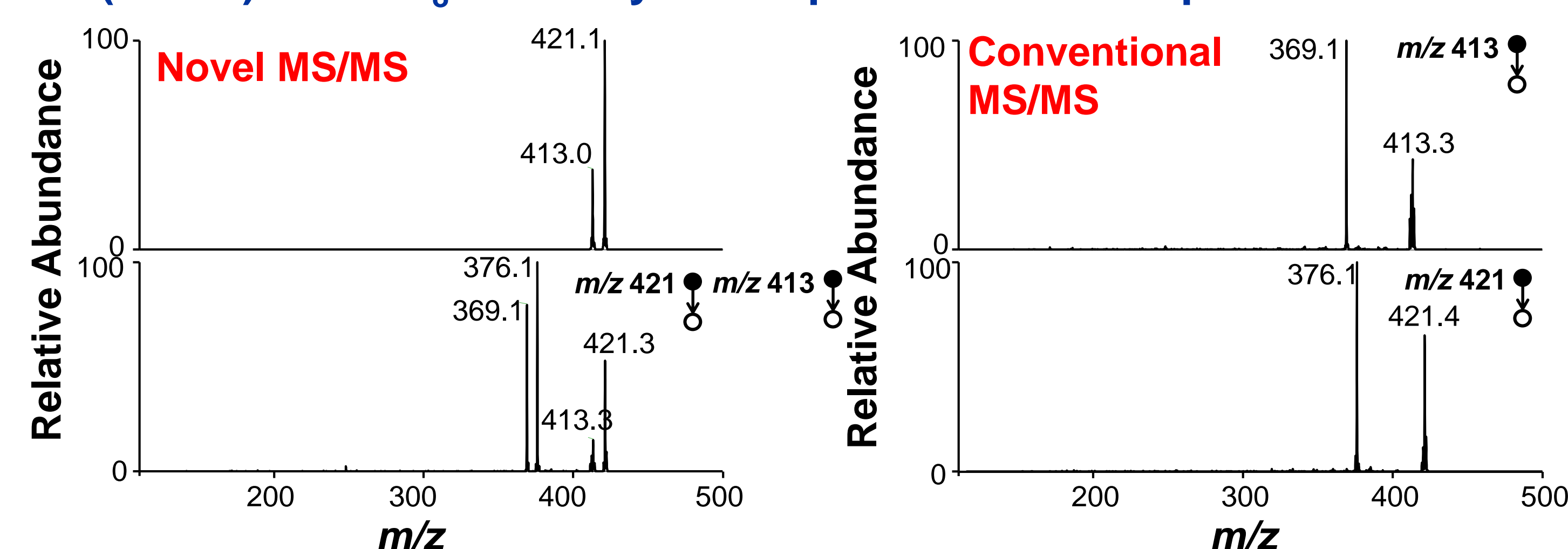


3. Prototype of All-in-one Ion Source



METHODS

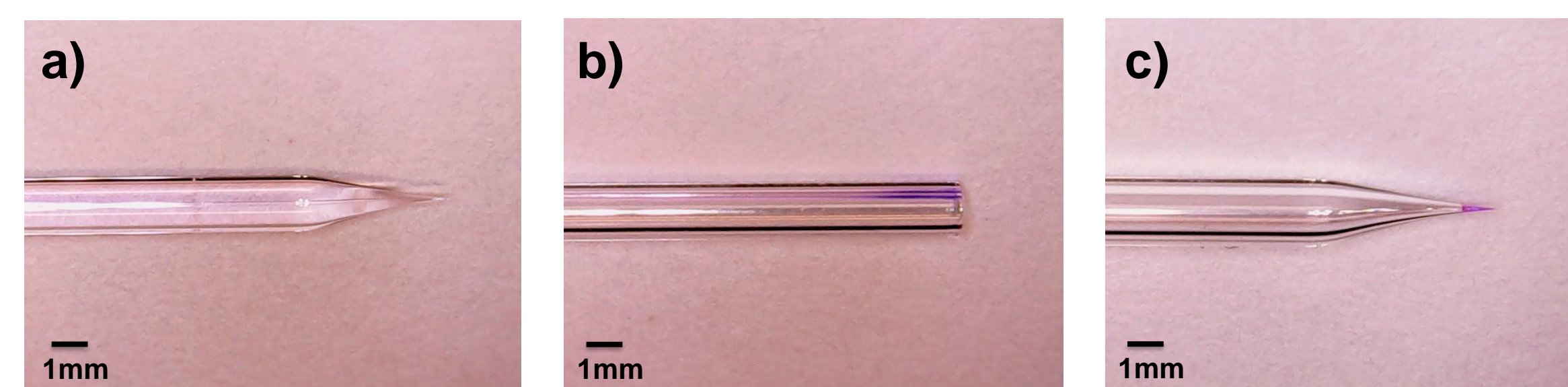
4. Novel Scan^[3] and Conventional Scan analysis of Perfluorooctanoic acid (PFOA) and ¹³C₈ PFOA by ion trap tandem mass spectrometer



RESULTS (I)

Pre-concentration

Figure 1. a) 10 μ L colorless dye solution in the glass emitter b) Deep purple stains at the edge of the glass emitter c) Preconcentrated purple solution at the tip of the glass emitter



10 μ L colorless purple dye solution dissolved in methanol was loaded into the glass emitter. Solvent was evaporated in 25min, deep purple stains were observed at the edge of the emitter. To reconstitute the dried dye, a drop of methanol was infused into the emitter by capillary action.

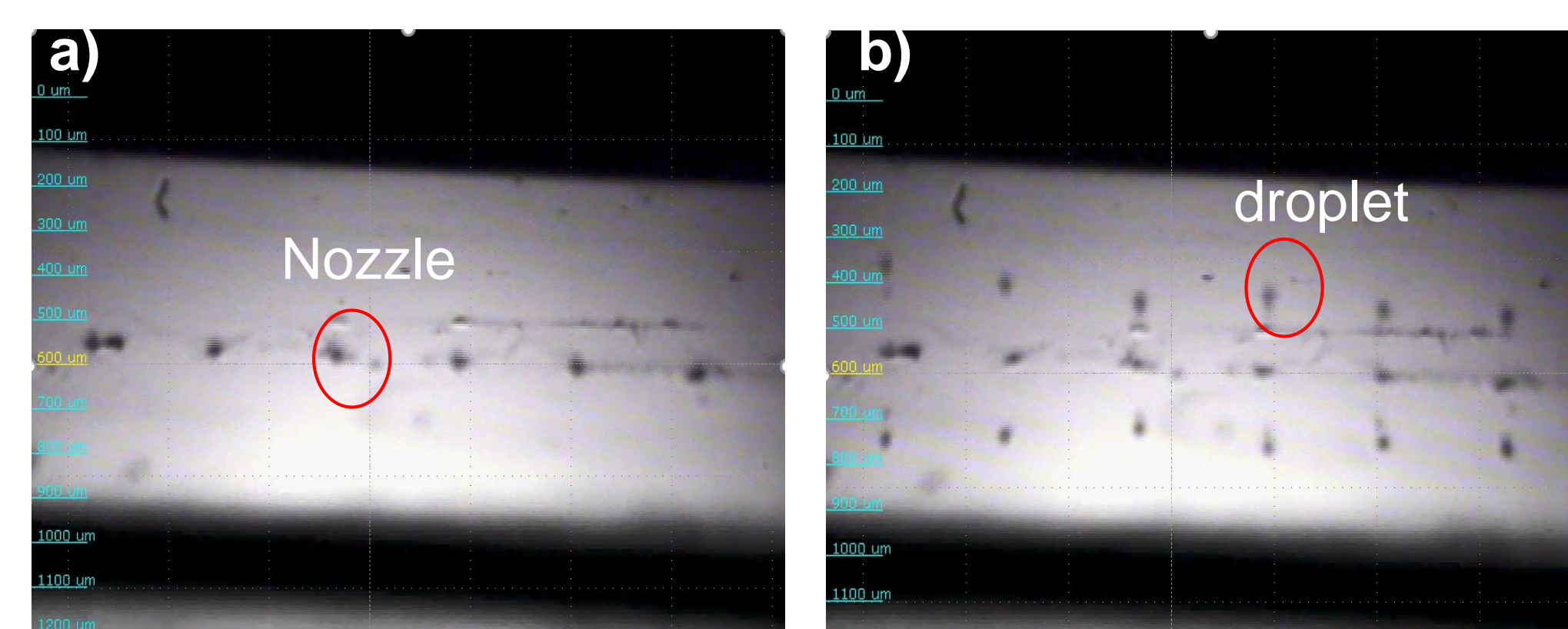
Table 1. Preconcentration factor of PFOA and PFOS in water samples

Trial #	1	2	3	4	5	6	Avg.
PFOS	170	250	250	90	30	90	147
PFOA	600	400	100	190	80	90	243

100 ng/L Perfluorooctanoic acid (PFOA) and Perfluorooctanoate sulfonate (PFOS) was spiked in pure water sample. All the samples were extracted by 200 μ L ethyl acetate. After extraction, 10 μ L ethyl acetate was loaded into the glass emitter and dried for the sequentially analysis. 10 μ g/L perfluoroheptanoic acid (PFHpA) and perfluorohexanesulfonic acid (PFHS) were used as internal standards.

Piezoelectric inkjet

Figure 2. a) The nozzles of inkjet w/o applying voltage b) The droplets generated by apply voltage pulses at a frequency of 2 kHz;

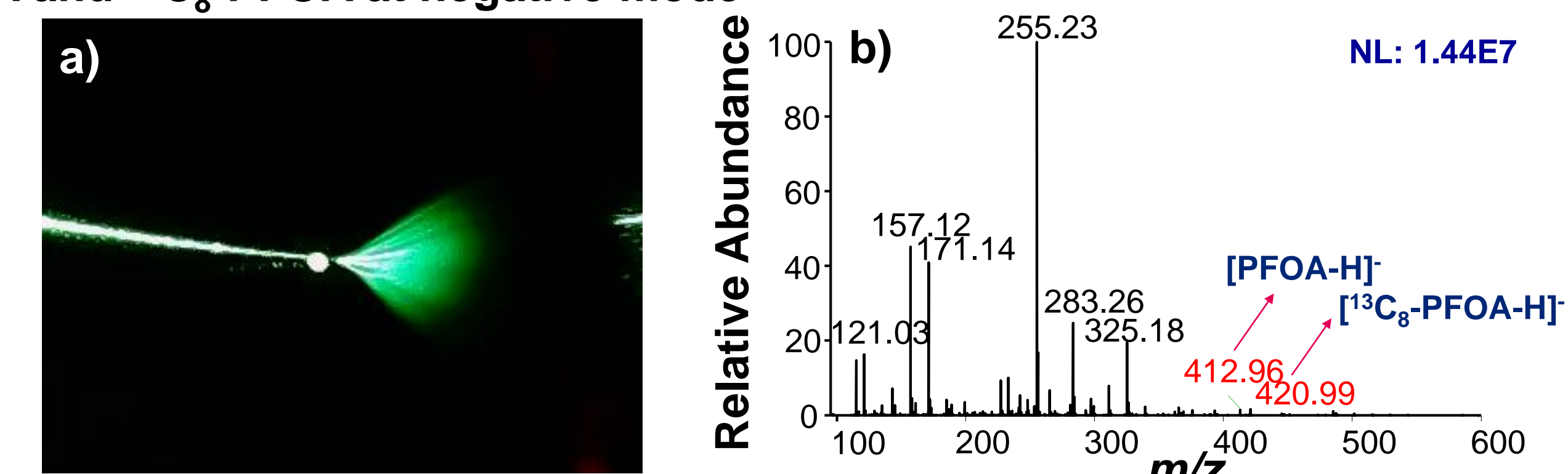


50% methanol/water was used as the ink. The frequency of the pressure pulse was 2 kHz. The diameter of nozzle is 16 μ m. The pulse width was 20 μ s, and the maximum voltage applied was 20 volts. Under these conditions, 2000 droplets were ejected per second and the volume of each droplet was 11 pL, the average velocity of droplets was around 2 m/sec.

RESULTS (II)

Ambient Contactless Relay ESI for nano-liter samples

Figure 3. a) Spray Plume of Relay ESI b) Mass spectrum of Full Scan of 0.1 μ M PFOA and ¹³C₈-PFOA at negative mode

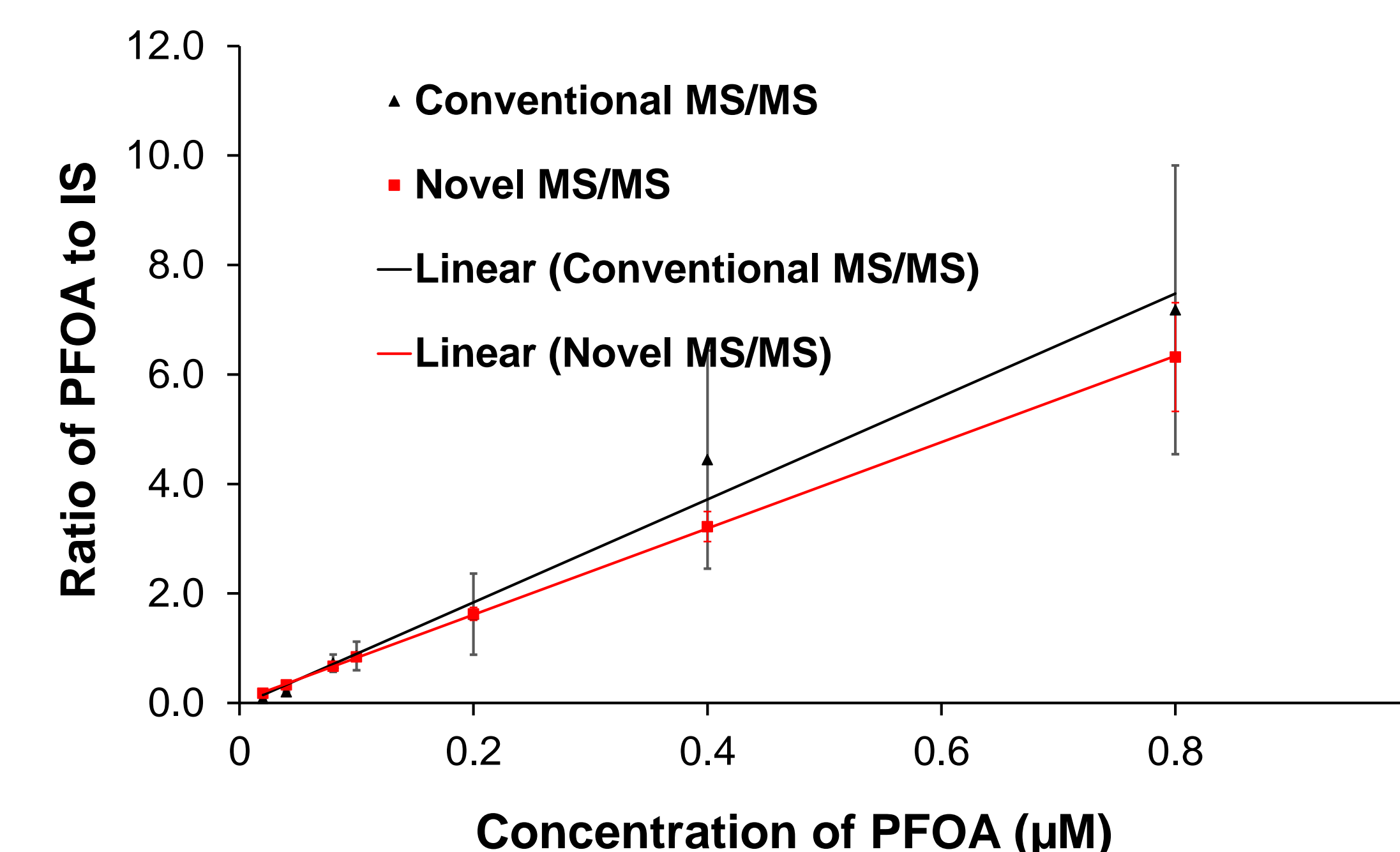


Novel Scan Function with Pulsed Ion Source

Table 2. Evaluation of precision of two scan modes at seven concentration points of PFOA with the relative standard deviation (RSD)

Scan Type	Concentration of PFOA (μ M)						
	0.02	0.04	0.08	0.1	0.20	0.4	0.8
Conventional MS/MS	12%	9%	22%	30%	46%	45%	37%
Novel MS/MS	5%	9%	9%	5%	7%	9%	16%

Figure 4. The calibration curves for the analysis of PFOA in the concentration ranging from 0.02 to 0.8 μ M. The high intense quantifier product ion m/z 369 of PFOA and m/z 376 of ¹³C₈-PFOA were used.



CONCLUSIONS

- Evaporation of μ L sample solutions achieved 100 folds of preconcentration.
- Ambient mechanical relay ESI was used to ionize nanoliter sample with stable spray plume.
- Compared with the conventional ion trap MS/MS scan, the novel MS/MS scan improved the precision of quantitative analysis significantly.

REFERENCES

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- Li, A. Y., Cooks, R. G., et al. *Angew. Chem. Int. Ed.* 2015, 54(23), 6893-6895.
- Li, L. F., Bailey, D. J. *Methods and Systems for Quantitative Mass Analysis*, US Patent 9911587

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