

Ion-Selective Membrane modified microfluidic paper-based solution sampling substrates for potentiometric heavy metal detection

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Contents

1. Experimental.....	2
1.1. Chemicals, materials, and electrodes.....	2
1.2. Preparation of ion-selective electrodes and microfluidic paper-based solution sampling substrates.	3
1.3. Potentiometric measurements with Pb ²⁺ -ISEs.....	3
1.4. Characterization of modified paper substrates.	4
1.5. Determination of lead(II) in environmental samples.....	5
2. Results and Discussion	6
2.1. Detailed FTIR analysis	9

1. Experimental

1.1. Chemicals, materials, and electrodes.

Analytical grade 3,4-ethylenedioxythiophene (EDOT), sodium polystyrene sulfonate (NaPSS), lead ionophore IV (tert-Butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide), 2-nitrophenyl octyl ether (o-NPOE), high molecular weight poly(vinyl chloride) (PVC), potassium tetrakis(4-chlorophenyl) borate (KTCIPB), nitrates of Mg^{2+} , Ca^{2+} , Na^+ , K^+ , Ba^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Cu^{2+} and Pb^{2+} , and tetrahydrofuran (THF) were purchased from Sigma Aldrich (Germany). All the aqueous solutions were prepared with ultra-pure water (18 M Ω cm resistivity) from Milli-Q Integral 10 Water Purification System, Sigma Aldrich (USA). Grade 388 quantitative cellulose filter paper was obtained from Sartorius (Germany) and utilized as the paper-based substrates. Glassy carbon (GC) disk electrodes with a Teflon body were purchased from X2Lab (Singapore). The reference electrode used was Ag/AgCl (3 M KCl) and obtained from BAS (Japan). The instrument calibration standard 2 for inductively coupled plasma-optical emission spectrometry (ICP-OES) was obtained from PerkinElmer, Inc. (USA).

1.2. Preparation of ion-selective electrodes and microfluidic paper-based solution sampling substrates.

Table S1. Composition of modifying solutions used for modification of paper substrates

Paper substrate	Membrane Components				
	PVC	o-NPOE	KTCIPB	Lead ionophore IV	THF
PS1.0	33.3 mg	-	-	-	2 ml
PS2.0	33.3 mg	65.2 mg	-	-	2 ml
PS3.0	-	65.2 mg	-	-	2 ml
PS4.0	-	-	0.5 mg	-	2 ml
PS5.0	-	-	-	1 mg	2 ml
PS6.0	33.3 mg	65.2 mg	0.5 mg	1 mg	2 ml

1.3. Potentiometric measurements with Pb²⁺-ISEs.

For the investigation of effect of different measurement configurations on the potential formation at the paper substrate | ISM interface only PS6.0 was investigated. The following configurations of PS6.0 coupled with Pb²⁺-ISEs were proposed and tested, namely in solution (standard beaker-based measurement), on PS6.0 in solution (the paper substrate touching ISM directly, while the whole set up was immersed in beaker containing sample solution), on PS6.0 (standard microfluidic paper-based solution sampling coupled with ISEs utilizing unconditioned PS6.0) and on conditioned PS6.0 (standard microfluidic paper-based solution sampling coupled with ISEs utilizing conditioned in respective standard solution for 30 min PS6.0) as shown in Figure S1.

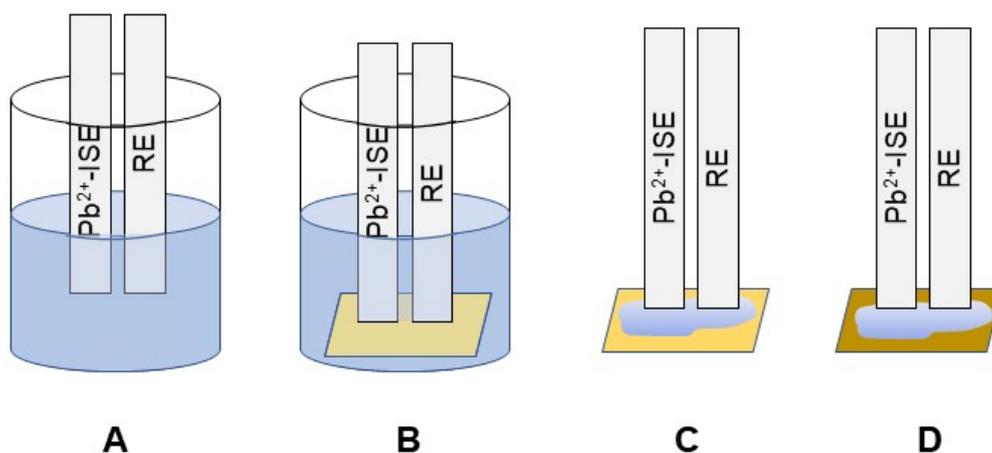


Figure S 1 Different measurement configurations used to investigate the potential formation at the paper substrate | ISM interface: in solution (A), on PS6.0 in solution (B), on PS6.0 (C) and on conditioned PS6.0 (D).

For the investigation of effect of conditioning the ISM modified paper substrates with primary ion (Pb^{2+}) on the potential formation at the Pb^{2+} -ISEs coupled with microfluidic paper-based solutions sampling, PS6.0 paper substrates were soaked first with different activities of lead(II) nitrate solutions ($10^{-1.42}$, $10^{-2.17}$, $10^{-3.06}$, $10^{-4.02}$, $10^{-5.01}$ M Pb^{2+}), washed with ultra-pure water, and dried before measurements. The paper substrates were subsequently used to register the EMF for standard solutions ranging from $10^{-4.02}$ to $10^{-2.2}$ M $\text{Pb}(\text{NO}_3)_2$. For the investigation of effect of interfering ion (Cd^{2+}) on the potential formation at the Pb^{2+} -ISEs coupled with microfluidic paper-based solutions sampling, PS6.0 paper substrates were soaked in 0.1 M $\text{Cd}(\text{NO}_3)_2$ for 30 min, washed with ultra-pure water, and dried before measurements. The same Pb^{2+} -ISE was then used for potentiometric measurements coupled with untreated PS6.0.

1.4. Characterization of modified paper substrates.

The surfaces and cross sections of unmodified and modified paper substrates were studied using a field emission scanning electron microscope (FESEM) (JSM-7600F, JEOL, Japan) along with energy dispersive X-ray spectroscopy (EDX). Samples were sputter coated with Pt for 20 s at 40 mA to obtain high quality images. The hydrophobicity of the paper substrates

was characterized by determining the contact angle using sessile drop method in Dataphysics OCA 15 goniometer (Germany). The dosing volume was set at 5 μL and dosing rate was set at 1 $\mu\text{L s}^{-1}$ for each deposition of a droplet of ultrapure water onto the paper substrate. Readings were taken on three different sites on the paper surface to determine uncertainty of the measurement ($n= 3$). Liquid absorption capacity of paper substrates was evaluated by immersing a $1 \times 1 \text{ cm}^2$ paper into ultra-pure water for 5 s and determining the mass change. Tensor 27 Fourier Transform infrared spectroscope (FTIR) operated in attenuated total reflection (ATR) mode was used to investigate the chemical changes in the paper substrate after modification. To do that, the paper substrates were crushed using mortar and pestle before investigation so that the sample could be homogenized instead of investigating only the surface properties of the paper substrates. The FTIR was also done on unmodified paper substrates.

1.5. Determination of lead(II) in environmental samples.

Three samples were prepared for the validation of the use of ISM modified paper substrates for solution sampling of high solid-to-liquid ratio complex environmental samples. A simulated chemical spill was prepared by adding a random amount of graphite powder into a lead(II) nitrate solution. The sample was named as “chemical spill”. A wet soil sample was prepared by spiking Pb^{2+} into raw soil collected from productive farmland in Singapore. The sample was named as “cultivation soil” sample. A sample originating from wetland area of the lake containing mostly algal growth and sediment was also collected. The sample was named as “wetland”. A random amount of lead (II) nitrate solution was used to spike all samples. Aside from samples that had high solid to liquid ratios, two more samples with complex solution composition were also studied. Two samples were leachates from different biowaste samples subjected to Toxicity Characteristic Leaching Procedure (TCLP) metal leaching procedure. The leachates were obtained according to the procedure: 100 g of biowaste was soaked in 2 L

of acetic acid solution and placed in a rotator rotating at 30 r min^{-1} for 18 h. The leachate was collected and filtered afterwards. The samples were named as “biowaste 1” and “biowaste 2”.

PS6.0 was coupled with Pb^{2+} -ISEs for the determination of Pb^{2+} in the complex environmental samples and the measurements were obtained as described in section 2.3. Aside of potentiometric determination, the total lead concentrations in all samples were determined using Perkin Elmer Optima 8300 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

2. Results and Discussion

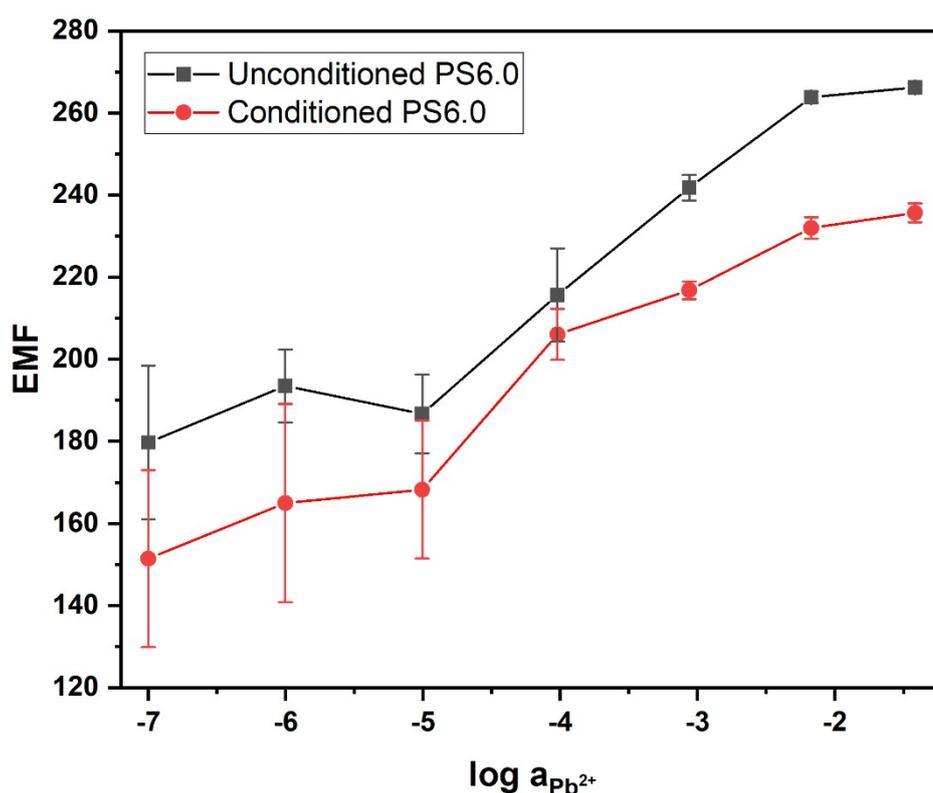


Figure S2 Potentiometric response of PEDOT(PSS) based electrode (without Pb^{2+} -ISM) coupled with unconditioned and conditioned (conditioned in $10^{-3} \text{ M Pb}^{2+}$ solution for 24 hours, washed with water and then dried) PS6.0

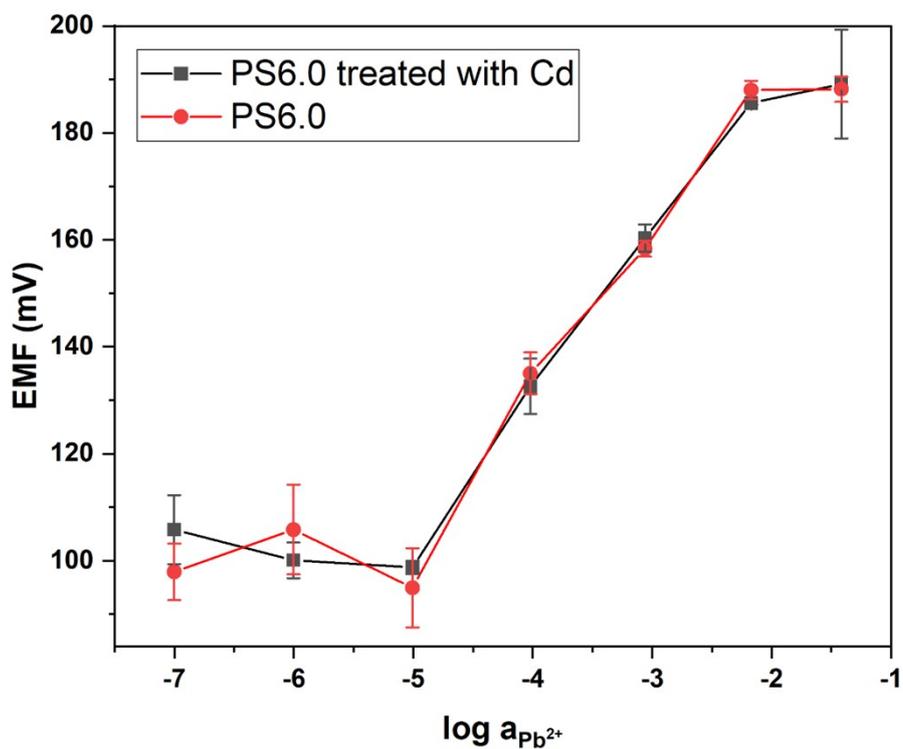


Figure S3. Potentiometric response of Pb²⁺-ISEs coupled with untreated PS6.0 and PS6.0 treated with 0.1 M Cd²⁺

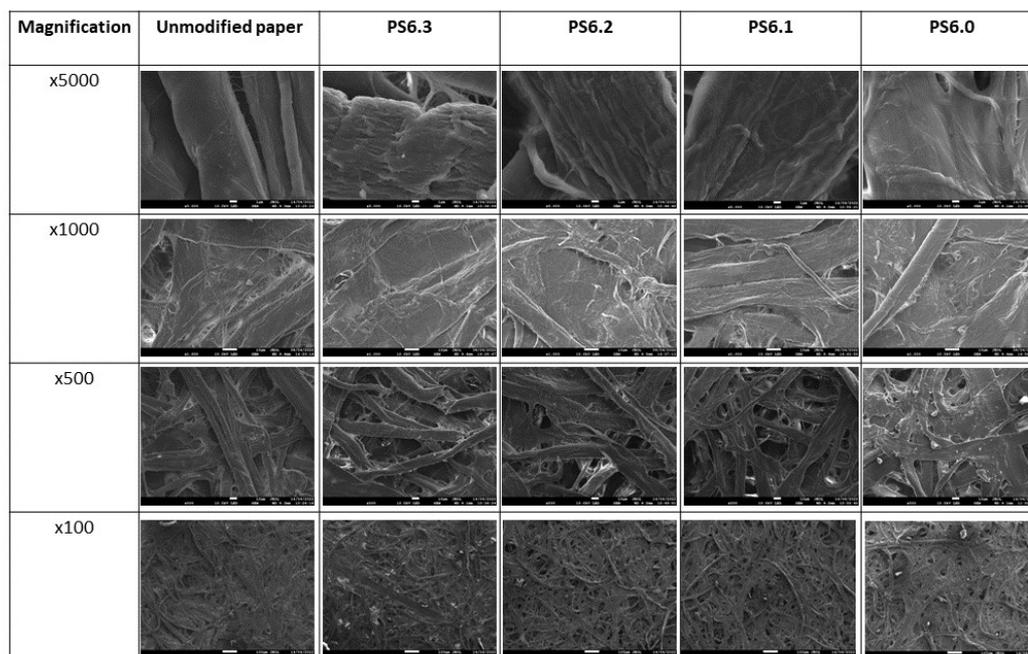


Figure S4. SEM images for ISM-component modified paper substrates at different magnifications

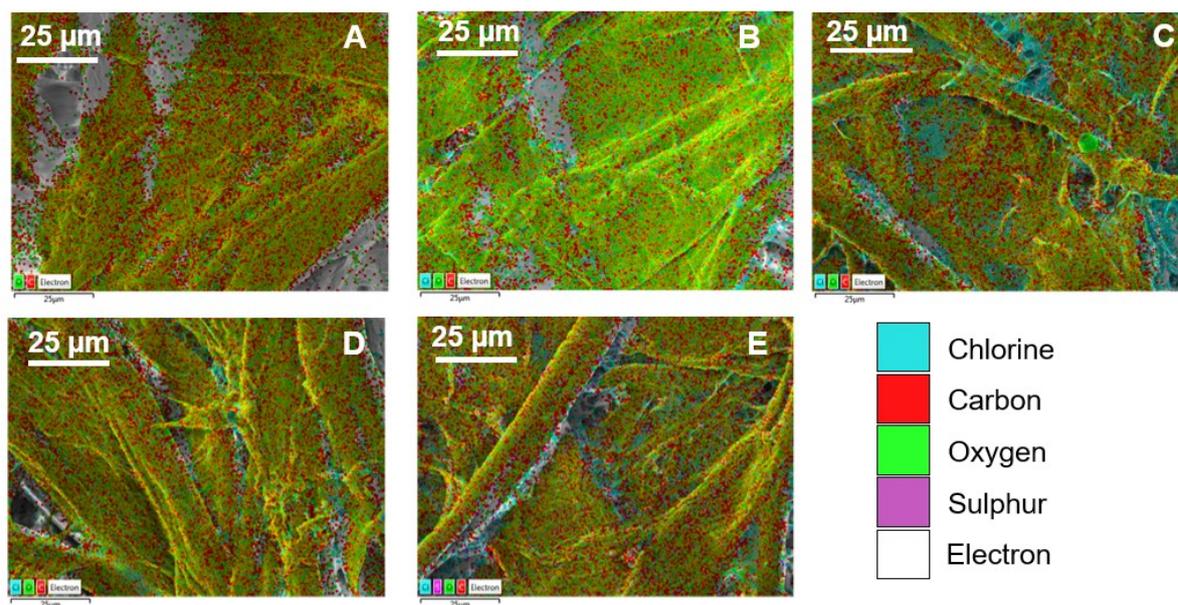


Figure S5. Elemental analysis of surface of unmodified paper (A), PS6.3 (B), PS6.2 (C), PS6.1 (D), and PS6.0 (E)

Detailed FTIR analysis

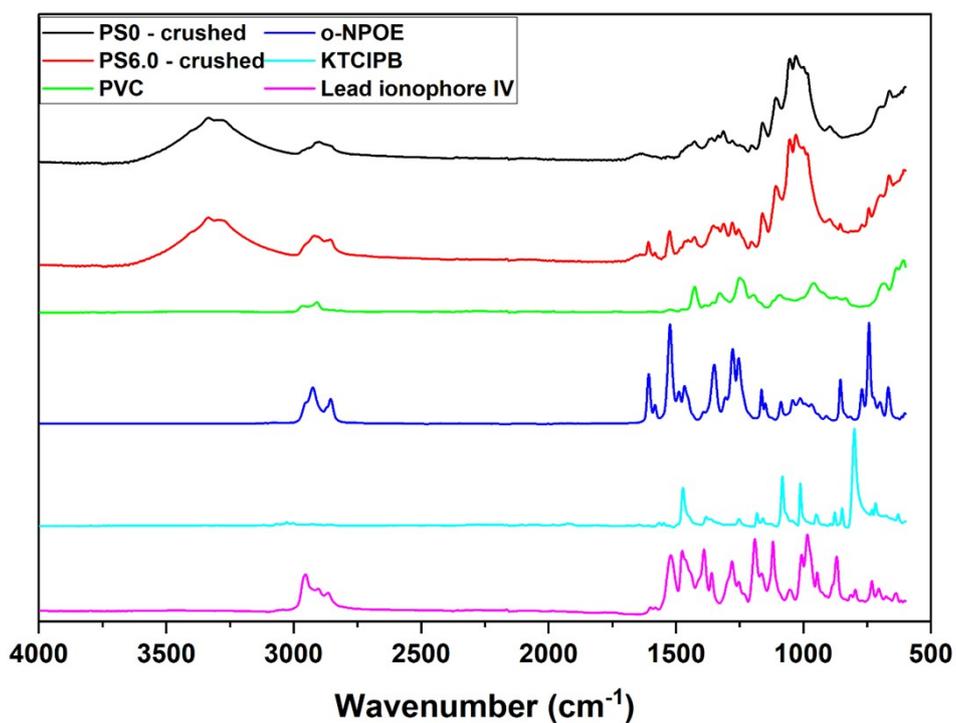


Figure S 6 FTIR of an unmodified paper substrate (PS0) as compared to PS6.0 and pure ISM-components.

Table S 2 Wavenumber regions and assigned functional groups

Origin	Group frequency, wavenumber (cm ⁻¹)	Assignment
O-H	3570–3200	Hydroxy group, H-bonded OH stretch
-CH ₂ -	2960-2850	methylene
C=C-C	1615–1580	Aromatic ring stretch
NO ₂	1525	Nitro
CH ₂ -Cl	1426	Angular deformation
CH-Cl	1254	Out of plane angular deformation
	900–670 (several)	Aromatic C-H
C-H	770-730+710-690	Monosubstitution (phenyl)
	770-735	1,2-Disubstitution (ortho)

Peaks observed at 3344 cm⁻¹ for both PS0 and PS6.0 indicates the presence of O-H functional groups in cellulose. A peak was observed at 2854 cm⁻¹ in the PS6.0 spectrum but absent in the PS0 spectrum. The peak at 2858 cm⁻¹ observed in the o-NPOE spectrum corresponds to -CH₂- group and suggests presence of similar group in PS6.0 since the wavelength range for -CH₂- group is 2960-2850 cm⁻¹. The peak at 2959 cm⁻¹ for lead ionophore IV could also be originating from the same group. Since o-NPOE contains an aromatic ring, the peak at 1605 cm⁻¹ can be attributed to an aromatic ring stretch and could also be the reason for the peak at 1607 cm⁻¹ for PS6.0. A peak appeared at 1526 cm⁻¹ (corresponding to NO₂ group) in both PS6.0 and o-NPOE spectra but absent in PS0 spectrum. Peaks at 1427 cm⁻¹ could be observed in both PS6.0 and PVC spectra, indicating presence of CH₂-Cl angular deformation. The peak observed at 1256 cm⁻¹ in PS6.0 spectrum and at 1254 cm⁻¹ in the PVC spectrum can be attributed to the CH-Cl out of plane angular deformation. Aromatic C-H group can be seen in a wide range of wavenumber and could be the reason for the peaks at 870 cm⁻¹ for lead ionophore IV and 854 cm⁻¹ for PS6.0. Peaks appearing in 700-770 cm⁻¹ region for both PS0, PS6.0, o-NPOE and lead ionophore (IV) spectra could arise from C-H groups (Monosubstitution and 1,2-Disubstitution).