Supporting Information

Paper-Based Potentiometric Ion Sensing

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Figure S1. (a) Schematic of a typical apparatus for potentiometric measurements. The reference electrode may have a more complicated double-junction construction. (b) and (c) Front view of paper components of a paper-based electrochemical device (EPAD). The paper was patterned by wax printing to define the inner reference zone, sample zone, central mixing zone, reference zone, and microfluidic channels. The reference zones include stencil-printed Ag/AgCl electrodes. The arrows with the same number as in (a) refer to similar functions.



Figure S2. (a) Fabrication of a PVC-based ion-selective membrane (ISM). (b) Photograph of a conventional ion-selective electrode with a PVC electrode body. The PVC-based ISM is located at the bottom of the electrode.



Figure S3. Photographs of mass fabricated paper-based potentiometric devices (ion-sensing EPADs) on one page of chromatography paper (20 cm by 20 cm in (a) and 20 cm by 16 cm in (b)).

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Cost of Ion-Sensing EPADs

We estimate the costs of paper materials and printing ink in single multilayer ion-sensing EPADs to be ~\$0.092. Ag/AgCl ink costs ~\$1 per gram, and one gram of ink is sufficient to produce 15 devices by manual stencil printing (\$0.067 per device). One page of wax-printed paper (20 cm by 20 cm, cost ~\$0.50), as shown in Figure S3, was used to print 28 bottom layers of the EPAD (\$0.018 per paper layer), or 72 top layers (\$0.007 per layer). We estimate that the costs of the paper and ink components for one device could be as low as \$0.06 using the Ag/AgCl ink as the electrode material and a graphite ink as the conducting material. The estimation above is based on the price of commercial products.

The total cost of the assembled device is largely determined by the cost of the ISM. For example, for a ~200 mg PVC-based K⁺ ISM, 66 mg poly(vinyl chloride) costs ~0.30; 132 mg *o*-NPOE costs ~0.88; 0.63 mg KTpClPB costs ~0.12; 2.85 mg valinomycin costs ~2.6; and 1.5 mL tetrahydrofuran costs ~0.1. Thus, the membrane costs ~4.0 in total when prepared from components provided by fine chemical suppliers in small quantities.

The dried ISM can be cut into five small membranes to be used in our paper devices. Each membrane costs ~\$0.8. The membrane cost for each measurement could be lowered by either further reducing the size of the paper zones, making thinner sensing membranes, performing multiple measurements on single ISMs, or taking advantage of lower material costs by bulk quantity purchasing.





Figure S5. Potentiometric responses of conventional ISEs (shown in Figure S2b) to (a) K^+ , (b) Na⁺, and (c) Ca²⁺. A 10⁻³ M KCl solution (for K⁺), a 10⁻¹ M NaCl solution (for Na⁺), and a 10⁻² M CaCl₂ solution (for Ca²⁺) were used as the inner reference solutions. A double-junction type external reference electrode (3.0 M KCl saturated with AgCl as the inner filling solution and 1.0 M LiOAc as the bridge electrolyte) or a Ag/AgCl reference electrode with 1 M KCl internal filling solution was used as the reference electrode.

