Electronic Supplementary Material (ESI) for Analyst.

Supporting Information for

Implementation of a Plasticized PVC-Based Cation-Selective Optode System into a Paper-Based Analytical Device for Colorimetric Sodium Detection

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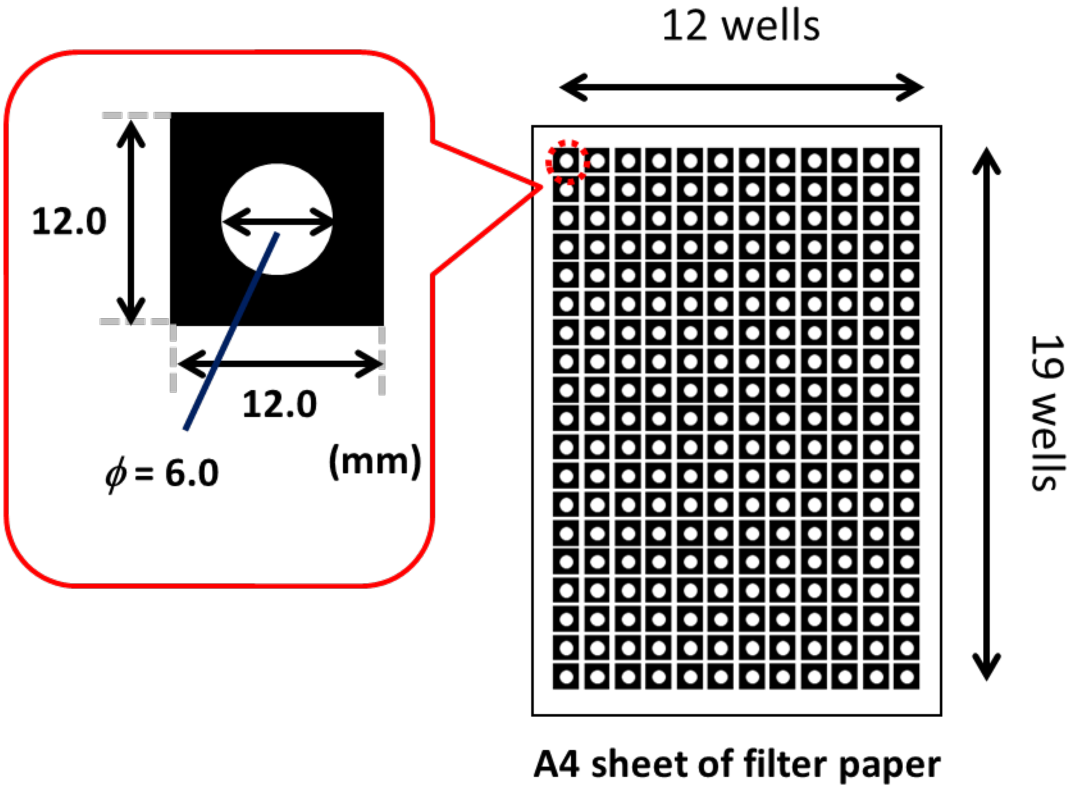

Figure S1. Schematic illustration of the wax barrier pattern printed on an A4 size filter paper sheet. The dimensions in the red box represent the settings in the PowerPoint graphic software.

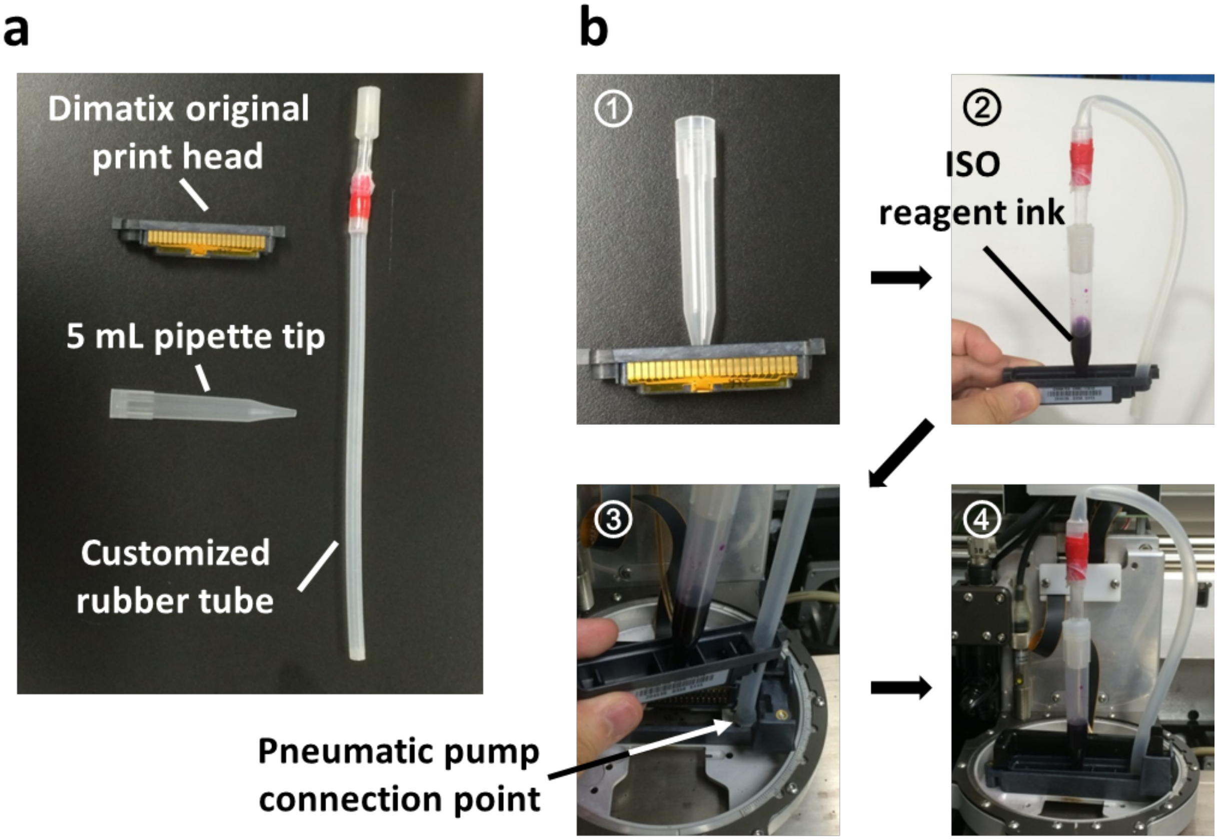

Figure S2. Detailed experimental setup for inkjet-printing of ISO reagent inks: (a) necessary materials including a Dimatix original print head, a 5 mL disposable pipette tip (Diamond chip D5000, Gilson, Middleton), a custom cut silicone rubber tube; (b) Images of the procedure for ISO reagent printing: 1) the pipette tip is attached to the Dimatix print head, 2) the pipette tip filled with the ISO reagent ink is connected to the silicone rubber tube, 3) the opposite end of the rubber tube is connected to the pneumatic pump of the Dimatix printer, 4) the Dimatix print head is mounted into the printer.

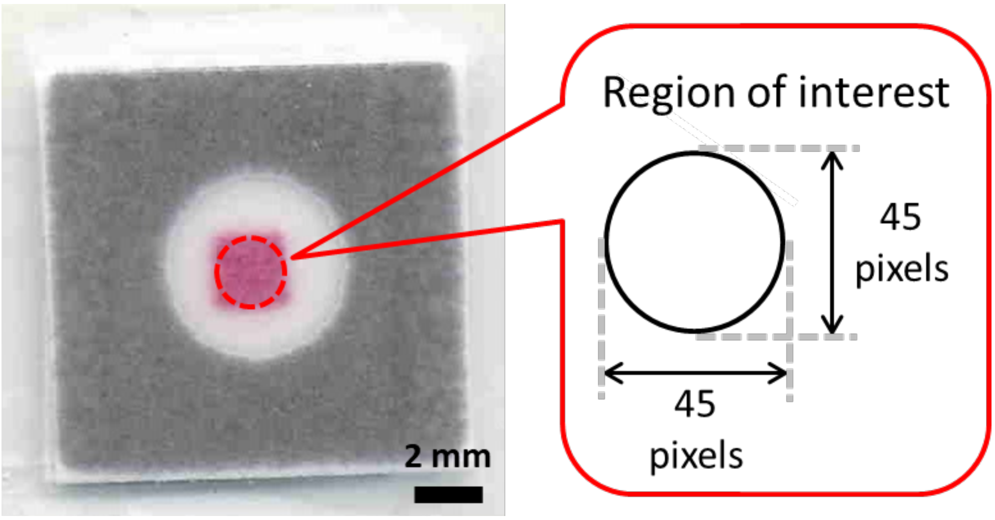

Figure S3. Colour measurement area on a scanned device image (600 dpi) for quantitative evaluation of ISO response. The dimensions of the ROI (region of interest) represent the settings in the ImageJ software.

Evaluation of ISO response based on the hue value

ISOs rely on an equilibrium cation-exchange reaction between the plasticized polymeric organic optode membrane phase containing the sensing reagents and the aqueous sample phase. The equilibrium reaction of the used ISO for Na^+ detection is given by eq. (S1):[1-2]

$$Na^+_{(aq)} + CH^+_{(org)} + L_{(org)} + R^-_{(org)} \leftrightharpoons H^+_{(aq)} + C_{(org)} + LNa^+_{(org)} + R^-_{(org)} \quad (S1)$$

where C is the chromoionophore (CH1), L the Na^+ ionophore (DD16C5), R^- the ion-exchanger (KTpClPB), and the indices "aq" and "org" indicate the aqueous sample phase and organic membrane phase, respectively. Extraction of the monovalent sodium ion (Na^+) into the organic membrane phase by the ionophore is accompanied by deprotonation of the chromoionophore in order to maintain the electro-neutrality within the optode membrane phase. The degree of deprotonation of the chromoionophore (α) is related to the activity of the target analyte ion (a_{Na^+}) in the aqueous sample phase as expressed by the following equation (eq. S2):[1-2]

$$a_{\mathrm{Na}^+} = \frac{1}{K_{exch}}\left(\frac{\alpha}{1-\alpha}a_{\mathrm{H}^+}\right) \times \frac{R_\mathrm{T} - (1-\alpha)C_\mathrm{T}}{L_\mathrm{T} - (R_\mathrm{T} - (1-\alpha)C_\mathrm{T})} \quad (S2)$$

Here, K_{exch} is the equilibrium constant of the reaction shown in eq. (S1), a_H the proton activity in the aqueous sample solution, R_T, C_T, and L_T the total concentration of ion-exchanger, chromoionophore and ionophore in the optode membrane, respectively. The optical property of ISOs is determined by the ratio of the chromoionophore's protonated and deprotonated form. The degree of deprotonation α of the chromoionophore is calculated according to eq. (S3) based on the experimentally determined absorbance of the chromoionophore in the optode phase: [1-2]

$$\alpha = \frac{A_{\mathrm{P}} - A}{A_{\mathrm{P}} - A_{\mathrm{D}}} \cdots \text{(S3)}$$

where A represents the experimentally measured absorbance at any given protonation state, and A_{P} and A_{D} stand for the absorbance in the fully protonated and deprotonated states, respectively.

Throughout this study, the hue value of the HSV (hue-saturation-value) colour coordinate system was used as the colorimetric signal of the vPADs. In analogy to eq. (S3), the hue parameter is linked to α by the following eq. (S4):[3]

$$\alpha = \frac{H_{\mathrm{P}} - H}{H_{\mathrm{P}} - H_{\mathrm{D}}} \cdots \text{(S4)}$$

Here H_{P} and H_{D} are the experimentally obtained hue values of the fully protonated and deprotonated chromoionophore, and H is the hue value at any given state. Throughout this work, H_{D} and H_{P} were measured by using aqueous solutions of 0.1 M KOH and 0.1 M HCl as the sample, respectively.

Detailed experimental procedure of ISO response curve fitting with theoretical sigmoidal function

K_{exch} was obtained by regression analysis with eq. (S2), using the Solver function of Excel (Microsoft) with the "GRG nonlinear system" Solver setting selected. The experimental parameters in eq. (S2) representing the activity of protons in the sample liquid phase ($a_{\mathrm{H^+}}$), as well as the concentrations of chromoionophore (C_{C}), ion exchanger (C_{R}) and ionophore (C_{L}) known from the optode phase composition, are shown in Table S1 below.

Table S1. Experimental parameters used for calculation of K_{exch}.

Parameters	Values
$a_{\mathrm{H^+}}$	1.0×10^{-6} mol/L
C_{C}	2.72×10^{-2} mol/kg
C_{R}	5.04×10^{-2} mol/kg
C_{L}	5.91×10^{-2} mol/kg

Optimization of the inkjet-printing cycles for ISO deposition onto filter paper

The experimental procedure is schematically shown in Figure S4a. Briefly, ISO membranes were inkjet-printed on an A4 sheet of filter paper without wax patterning. After printing, the paper was cut (ϕ = 5 mm) with a craft punch (Carla Craft CP-01 1/8, Carl, Tokyo, Japan), and the side with the printed ISO membrane was laminated (refer to the "cross section" schematic in Figure S4a). 50 μL of pH-buffered NaCl solutions (50 mM MES-TMAOH, pH 6.0) were applied to the ISO-printed paper disc, followed by incubation for 20 min for colour development. Finally, the residual sample liquid was removed by a paper towel, and the ISO-printed side of the paper discs were scanned immediately.

Figure S4b shows the Na^+ concentration-dependent colorimetric response of the ISO membranes for various numbers of printing cycles. All cases resulted in a visually observable colour change from blue to pinkish red. However, the weak colour obtained after 10 printing cycles did not allow reproducible hue-based quantitative analysis, because of the incompatibility of the hue value with colorless (or nearly colorless) spots. The quantitative evaluation of the ISO response after 20, 30, 40 and 50 printing cycles is shown in Figure S4c with the hue-based signal converted to the deprotonation degree (α). Considering the fact of no significant difference of ISO response characteristics (K_{exch} values) when comparing between 20-50 printing cycles and little enhancement of colour intensity above 30 printing cycles observed in Figure S4b, 30 printing cycles were adopted as the optimal ISO ink deposition amount throughout this work.

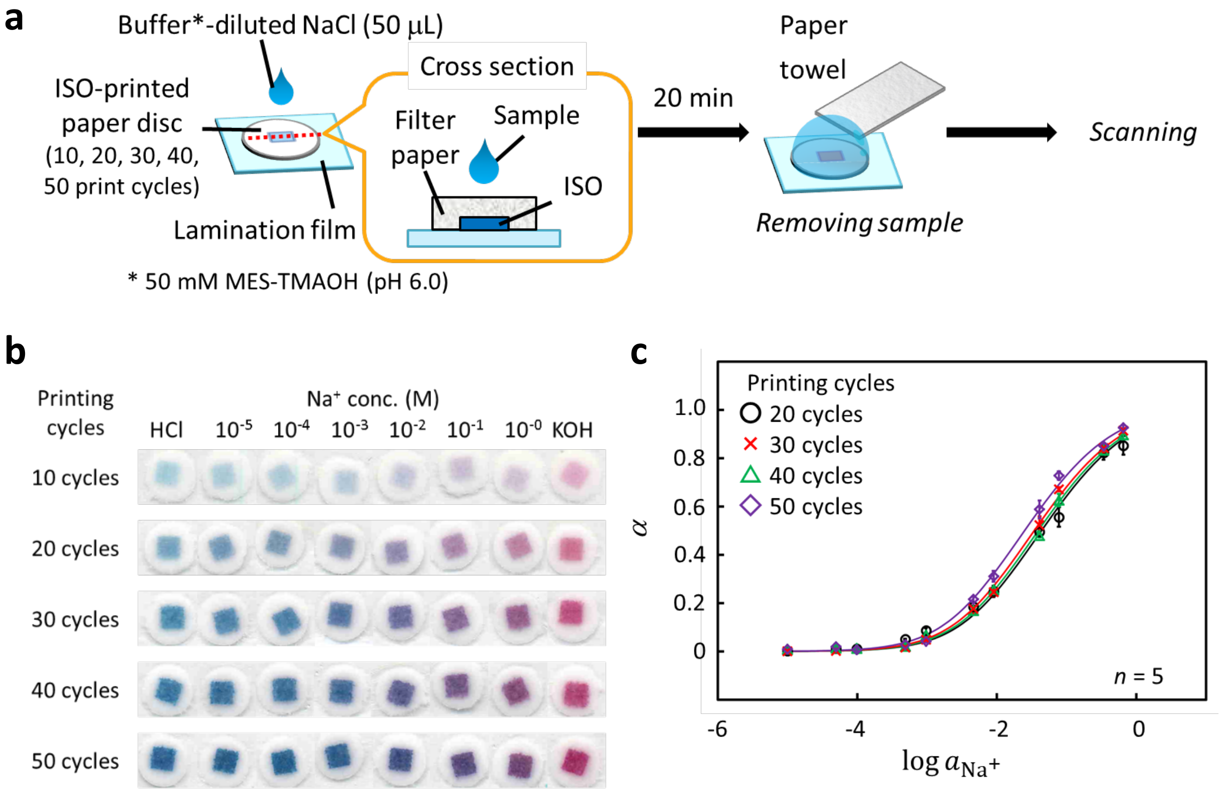

Figure S4. (a) Experimental procedure for optimization of ISO inkjet-printing cycles based on a spot test; (b) Scanned images of paper-based ISOs at 10, 20, 30, 40, 50 printing cycles after exposure to various concentrations of Na^+; (c) Hue-based (converted to α) response curves obtained by scanning the results of 20, 30, 40, 50 printing cycles shown in part (b); each data point has been obtained by measurements with 5 individual single-use paper discs; error bars indicate the standard deviations.

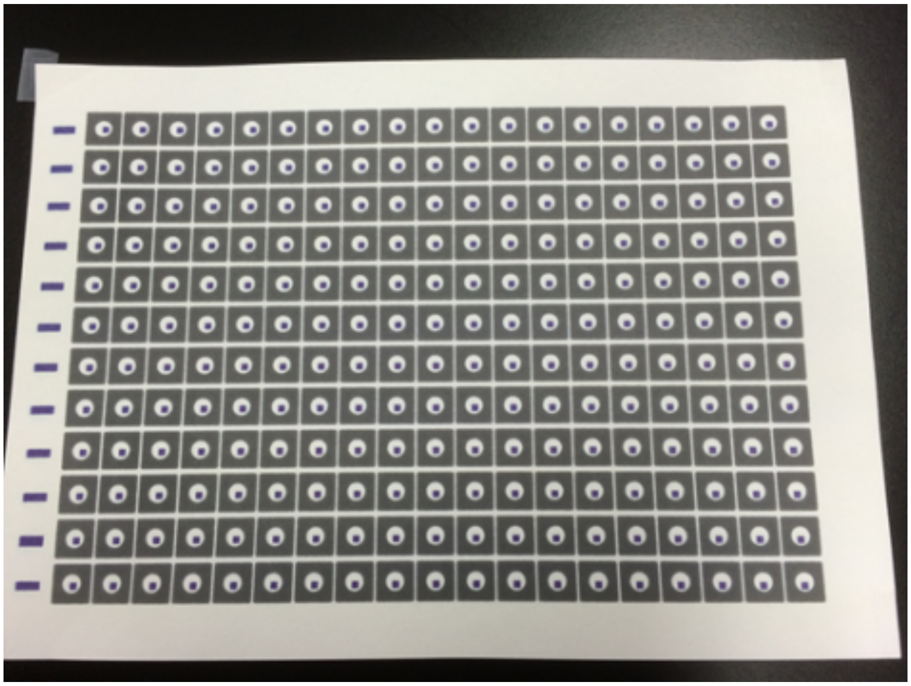

Figure S5. Photograph of ISOs inkjet printed on a wax-patterned A4 size filter paper.

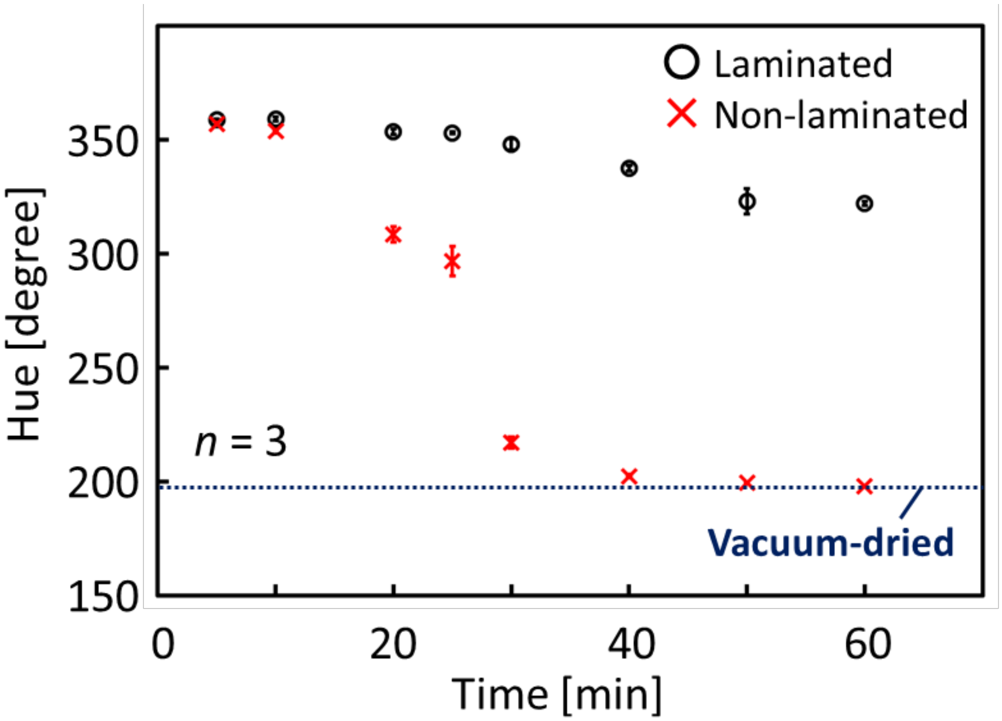

Figure S6. Quantitative evaluation of the wetting state of the bottom paper layer of laminated and non-laminated devices as shown in Fig. 3 of the main text (application of 15 µL of 0.3 g/mL aqueous $CoCl_2$ solution to sample inlet followed by scanning after indicated time); the "vacuum-dried" result represents the completely dry state; each data point has been obtained by measurements with 3 individual single-use devices; error bars indicate the standard deviations.

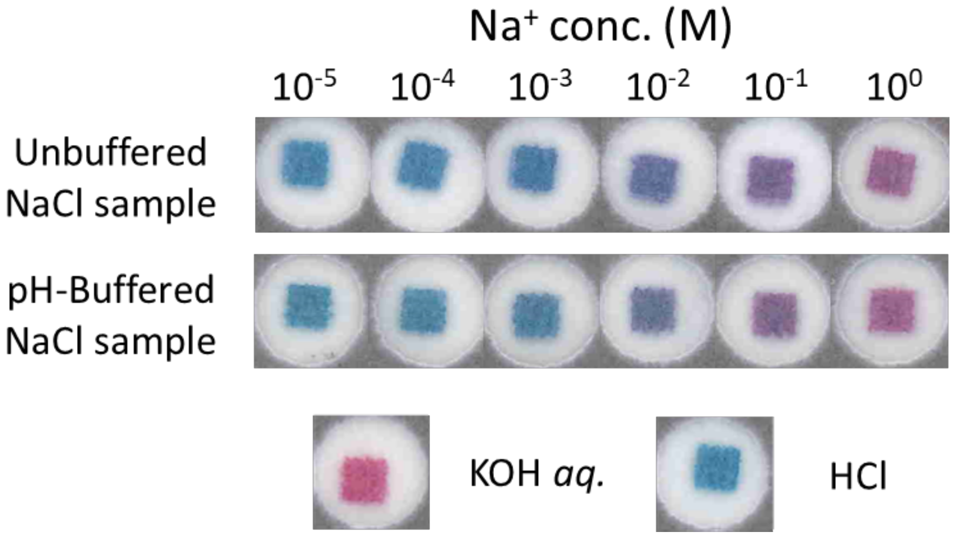

Figure S7. Validation of the pH-buffering function of vPADs: colorimetric ISO response observed after the application of aqueous NaCl solutions to devices integrating the buffer component (upper row) and pH-buffered (50 mM MES-TMAOH, pH 6.0) NaCl solutions to devices lacking the buffer component (bottom row). The corresponding hue-based response curves are given in Figure 4 of the main text. Colours for the fully deprotonated and fully protonated states of the chromoionophore were obtained by application of 0.1 M KOH and 0.1 M HCl, respectively, to the devices.

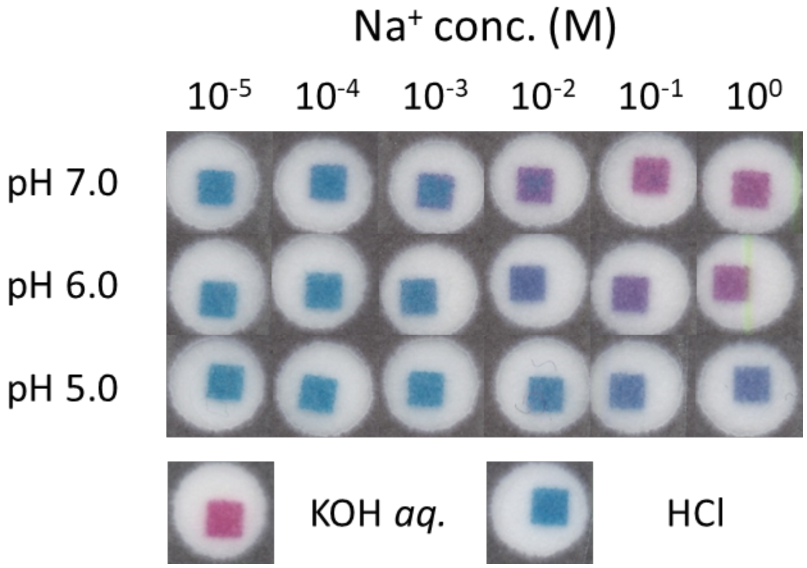

Figure S8. Colorimetric vPAD ISO response at various pH-values obtained by application of unbuffered aqueous NaCl solutions to devices integrating different buffer components. The corresponding hue-based response curves are given in Figure 5 of the main text. Colours for the fully deprotonated and fully protonated states of the chromoionophore were obtained by application of 0.1 M KOH and 0.1 M HCl, respectively, to the devices.

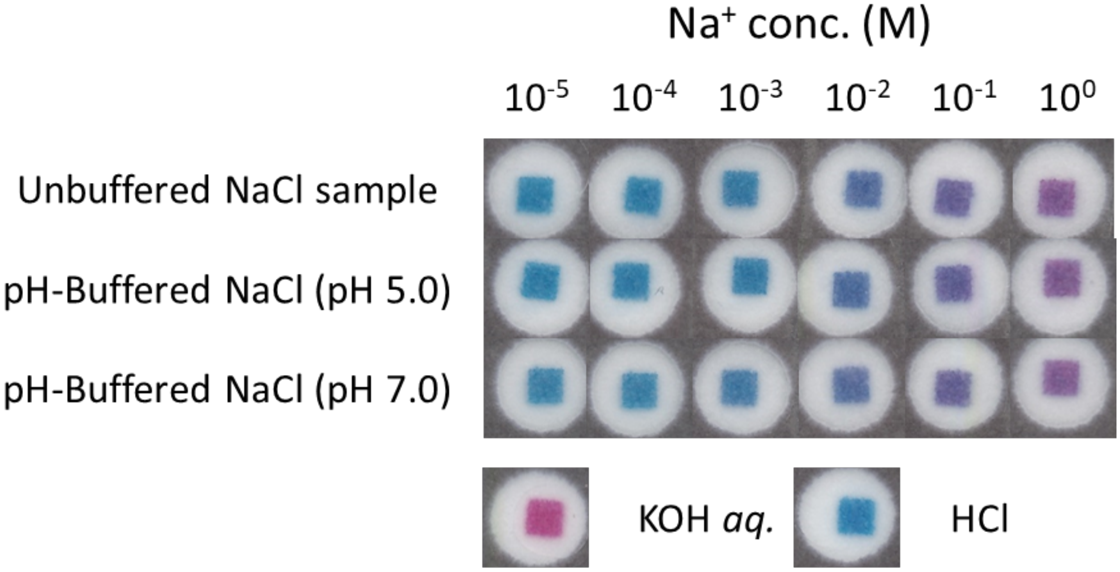

Figure S9. Colorimetric vPAD ISO response obtained by application of aqueous NaCl solutions of different pH values (unbuffered, 10 mM citric acid-TMAOH pH 5.0, 10 mM HEPES-TMAOH pH 7.0) to devices integrating pH 6.0 buffer components. The corresponding hue-based response curves are given in Figure 6 of the main text. Colours for the fully deprotonated and fully protonated states of the chromoionophore were obtained by application of 0.1 M KOH and 0.1 M HCl, respectively, to the devices.

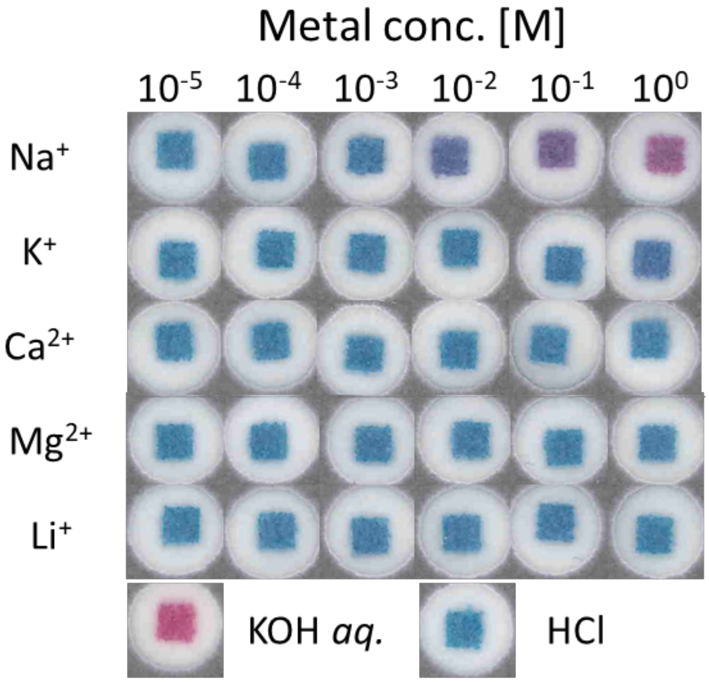

Figure S10. Colorimetric vPAD ISO response to various unbuffered alkali and alkaline earth metal cation solutions (chloride salts) obtained on devices with integrated pH-buffering function (pH 6.0). The corresponding hue-based response curves are given in Figure 7 of the main text. Colours for the fully deprotonated and fully protonated states of the chromoionophore were obtained by application of 0.1 M KOH and 0.1 M HCl, respectively, to the devices.

Calculation procedure for optical selectivity coefficient over K^+

Figure S11 shows the response behavior of the ISO vPADs to Na^+ (black data set) and K^+ (red data set) in the logarithmical activity range between -5 and 2. According to each sigmoidal fitting curve, 50% deprotonation of the chromoionophore (*i.e.* $\alpha = 0.5$) by Na^+ and K^+ is achieved at activities of $\log a_{\mathrm{Na}^+} = -1.01$ and $\log a_{\mathrm{K}^+} = 1.09$, respectively, resulting in a logarithmic selectivity coefficient for Na^+ over K^+ of $\log K_{Na,K}^{opt} = -2.10$.

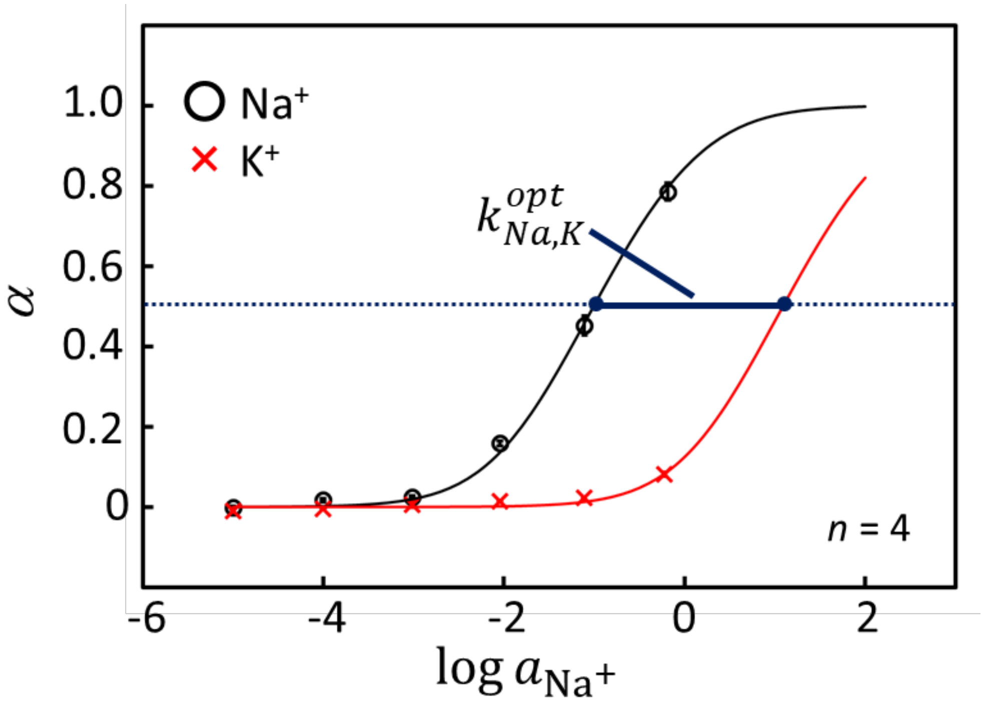

Figure S11. ISO response curves for Na^+ (black data set) and K^+ (red data set) obtained on vPADs with integrated pH-buffering function (pH 6.0); sample volume 15 µL; equilibration time 20 min; each data point has been obtained by measurements with 4 individual single-use devices; error bars indicate the standard deviations.

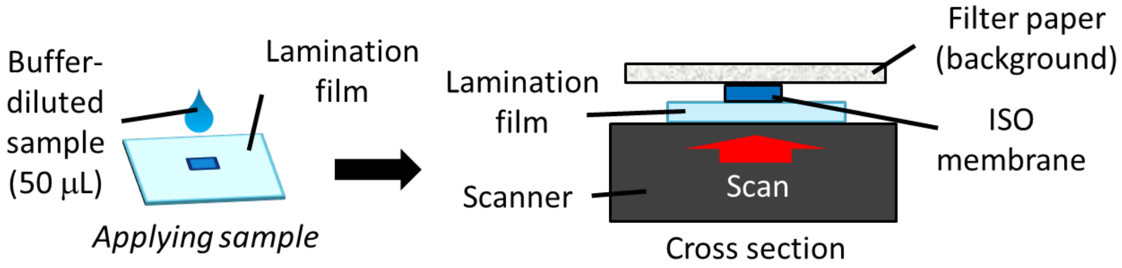

Figure S12. Experimental procedure for the spot test with classical membrane-type optodes on a lamination film. The ISO membranes were first prepared on an A4 sheet of lamination film with the Dimatix DMP-2831 inkjet printer in the same way as on the filter paper platform. 50 µL of aqueous NaCl solutions prepared in MES-TMAOH buffer (pH 6.0, 50 mM) were directly applied to the ISO-printed lamination film. After 20 min of equilibration, the remaining sample liquid was removed with a paper towel, and the ISO-printed lamination film was scanned from the bottom side against a filter paper background, simulating the vPAD arrangement.

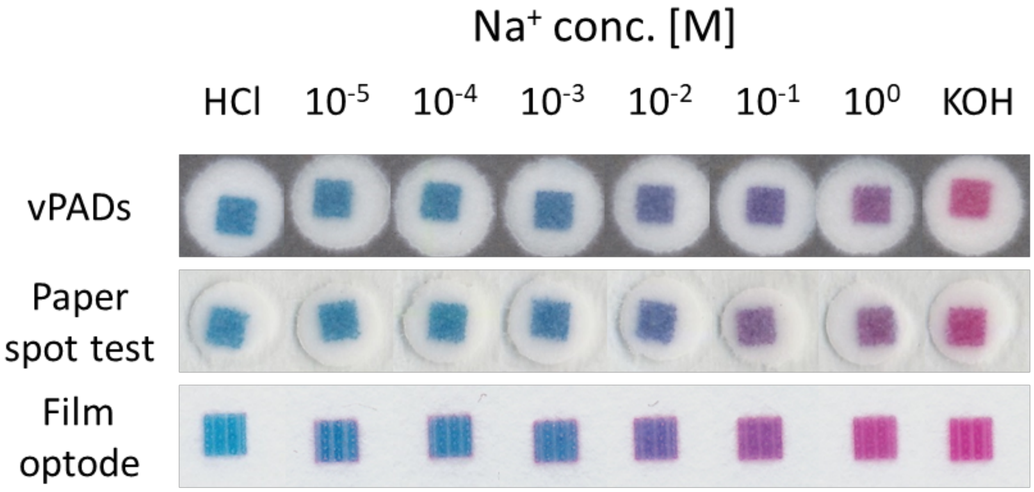

Figure S13. Colorimetric ISO response to unbuffered Na^+ solutions obtained on devices with integrated pH-buffering function (vPADs, pH 6.0) and to buffered Na^+ solutions (50 mM MES-TMAOH pH 6.0) obtained with paper spot tests and film optodes prepared on lamination film. The corresponding hue-based response curves are given in Figure 9 of the main text.

Experimental procedure of acid-base titration for calculating ion-exchange capacity (IEC) of filter paper

Vacuum-dried chopped pieces of filter paper were soaked in 20 mL of 0.01 N NaOH solution during 1 h at room temperature. Then, 10 mL of the resulting solution was titrated against a 0.01 N HCl standard solution ($f = 1.001$) using a pH-meter for endpoint indication. The ion-exchange capacity (IEC) of the filter paper was calculated according to eq. (S5).[5]

$$\mathrm{IEC_{paper}}\ [\mathrm{mmol/kg}] = \frac{0.01\ [\mathrm{mol/L}] \times f_{\mathrm{NaOH}} \times (10\ [\mathrm{mL}] - V\ [\mathrm{mL}]) \times 2 \times 1000}{m\ [\mathrm{g}]} \cdots \text{(S5)}$$

where f_{HCl} is the factor of the 0.01 N HCl titrant standard (1.001), V is the amount of 0.01 N HCl used to neutralize the sample solution, and m the mass of the filter paper after vacuum drying for 1 h.

Table S2 Mass of filter paper and ion-exchange capacity (IEC) of filter paper. Experiments were performed on different days.

Factor of NaOH aq. (f_{NaOH}) [-]	Amount of 0.01 N HCl (V) [mL]	Mass of vacuum-dried filter paper (m) [g]	IEC of filter paper [mmol/kg]
0.961	8.7	1.562	16.00
0.921	8.1	1.532	15.62
0.971	8.7	1.559	16.20
		Average	15.94±0.24

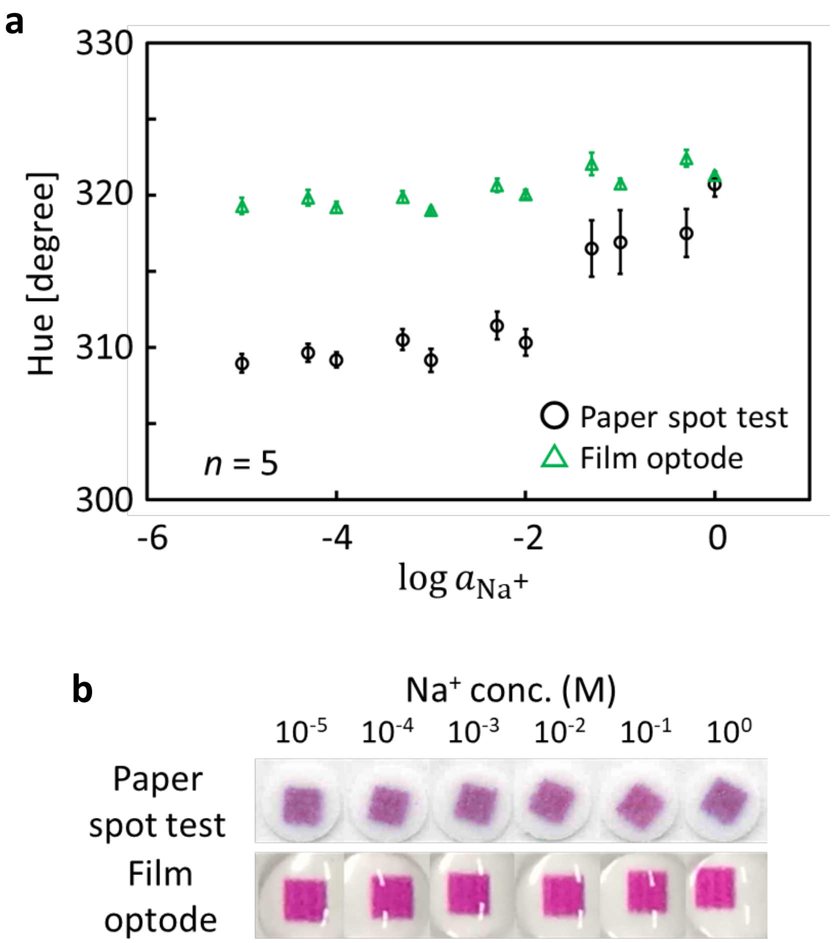

Figure S14. Response behaviour of spot tests with ISO membranes deposited onto filter paper (top row) or lamination film (bottom row) in the absence of anionic additive (KTpClPB) exposed to pH-buffered (pH 6.0) NaCl solutions: (a) hue-based response curves and (b) corresponding images acquired with a colour scanner (paper) or an iPhone 5S (film); sample volume 50 μL; equilibration time 20 min; each data point has been obtained by measurements with 5 individual spots; error bars indicate the standard deviations.

References

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