Quality Evaluation of Art Materials

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Successful usage of electrical conductance measurements in finding optimal pigment concentration for water-based ink is presented. Other possible applications of the approach are discussed.

KEYWORDS: Conductance, Ink, Pigment, Printing, Concentration.

Introduction

Most of the art materials for painting and printing are comprised of pigment components dispersed in some solvent components. The very key question which manufacturers and artists ask with respect to any such material is:

What is the best pigment-to-solvent ratio (if any)?

Concept of best concentration

At the very beginning a term *best concentration of pigment* must be clarified. Manufacturer is keen to find such a magical pigment concentration, which would provide his/her product with following major properties altogether:

- Exact color representation.

  For instance, black ink should be as black as possible. To meet this demand, concentration of pigment must not be too high as to prevent adverse agglomeration.

  N.B.: Color misrepresentation is very often caused by pigment agglomeration.

  The phenomenon brings additional unwanted color tints that are due to the secondary optical effects such as interference and total internal reflection.
- Sufficient covering power.

  In this case concentration of pigment must not be too low.
- Predictable rheological properties.

  This feature is especially sought-after in producing inks for jet printing.

  Once again, agglomeration would make all attempts to tailor ink properties futile. For this reason, concentration of pigment must not be too high.

Artist would gain additional controls over material by knowing its *best concentration of pigment*:

- Ability to produce most vivid yet translucent strokes/washes any time he/she paints with any material at hand.

- Opportunity to run an express comparison between similar materials offered by different manufacturers with no wasting precious resources on trial-and-error approach.

Analysis of the wishlist above allows one to define *best concentration of pigment* as the highest possible agglomeration-free pigment concentration. Based on this definition, ***best pigment concentration is*** rather being called ***the highest working concentration of pigment (HWCP)***.

Here, a method of electrical conductance measurements is shown to be an effective mean in finding HWCP for water-based ink system.

Method

Let us try anticipating a trend the conductance follows while pigment concentration increases in pigment-water system (Fig. 1).

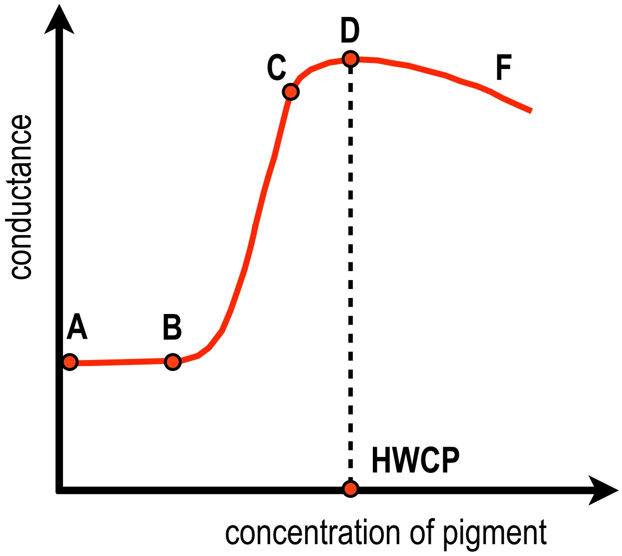

Figure 1. Typical conductance curve.

region A-B

Concentration of pigment is low. Single pigment particles are entirely separated from each other with highly resistant distilled water. For this reason, a conductance of the whole system is small and almost constant.

region B-C

This is a so-called *percolation* region. Conductance of ink drastically increases due to formation of a 3-D network built from the pigment particles which are much more conductive than distilled water.

It should be noted here that every point of contact between pigment particles inevitably contributes to the rise of resistance of the system. However, the growth and branching of conductive paths are the most prevailing processes in this region.

region C-D

Rate of path formation and branching decreases because of the space limitations. Growth of the conductance is slowing down.

region D-F

No more formation of new conductive paths. No more additional branching. Pigment concentration keeps on growing, though. That is why pigment material is forced start agglomerating. Rise of the number of particle-particle contacts leads to conductance fall.

From the phenomenological description one can conclude that beyond point D (Fig. 1) agglomeration becomes dominant process. Thus, concentration of the pigment, which corresponds to the biggest conductance of the system, might rightfully be assigned to HWCP (Fig. 1).

Experimental set up

As a proof of concept, point of the biggest conductance (PBC) was determined for black ink of one commercially available brand. For this purpose, three consecutive sets of conductance measurements were done using homemade electrochemical cell (e.cell) and ohmmeter. The results were plotted and analyzed then (Fig. 2). Detailed information about materials, instruments, code, etc. one can find in Supplementary Information.

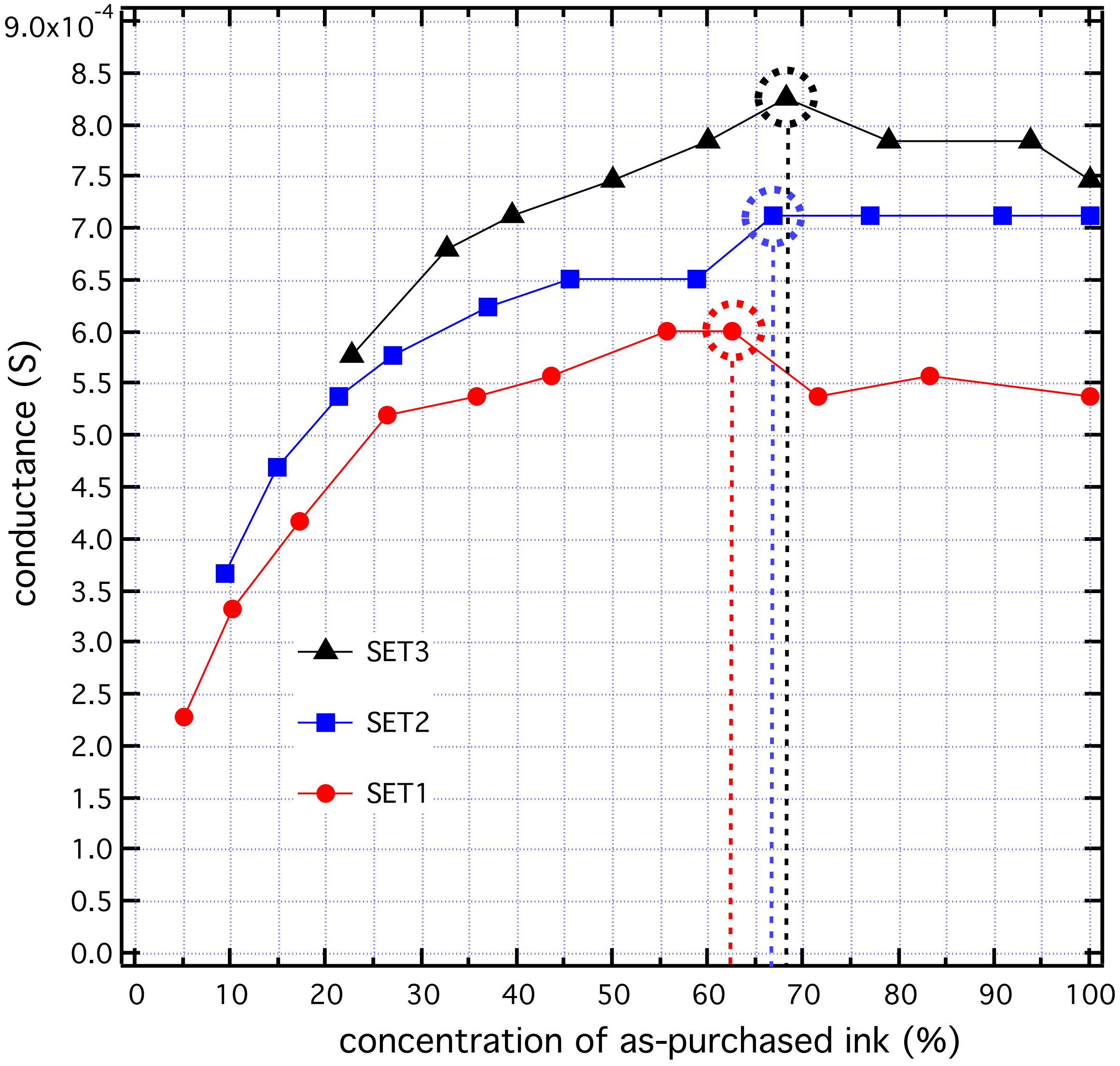

Figure 2. Conductance vs. concentration curves for ink aqueous solutions.

Discussion

Results of the measurements are presented in Figure 2. PBCs are marked with dotted circles.

One can easily notice that x & y values for PBC in set 2 are larger than that for set 1, and in set 3 are larger than that for set 2. This trend in shifting values from set to set can be explained by temperature increase in the lab room during the experiment. Indeed, it is well-known that electrical conductance of the solutions is very sensitive to temperature changes [1]. Measurements started at lab temperature ≈ 19 ºC and were performed following the sequence: set 1 → set 2 → set 3, while temperature in the lab was naturally rising all the time.

For this reason, to stay on the safe side, concentration of as-purchased ink of 60% was taken as one, which is for sure approaches HWCP at temperatures 20 ºC plus. To test ink at ≤ HWCP (labeled as “60%”) in comparison with as-purchased ink (labeled as “100%”) both samples were applied to watercolor paper in altering stripes’ pattern using “wet-on-dry” technique (Fig. 3).

As one can see, “60%” stripes look blacker and give no highlights at any angle, compared to “100%” stripes (Fig. 4).

N.B.: According to the label, as-purchased black ink comprises of pigment, water, and *glycerin* of unspecified concentrations. For this reason, control experiments with “60%” samples, containing glycerin of the same concentrations as “100%” samples are left to discretion of manufacturer.

To find lowest working concentration of pigment (LWCP), samples with descending concentrations of as-purchased ink were applied in stripes’ pattern to watercolor paper (Fig. 5). It is easy to notice that covering power of the ink considerably decreases below “54%” – starting from “48%” stripe (Fig. 5).

Thus, optimal concentrations of the pigment in this ink lie in the range 54% - 60% of its content in as-purchased product.

On the other hand, ink can readily be used as a painting material in substitution of much more expensive watercolor paint. In this respect see, for instance, bravely innovative sketches by Rembrandt van Rijn [2]. Concerning material under the study, solutions of 6%, 18%, and 30% are well suited for 4-value painting in monochrome.

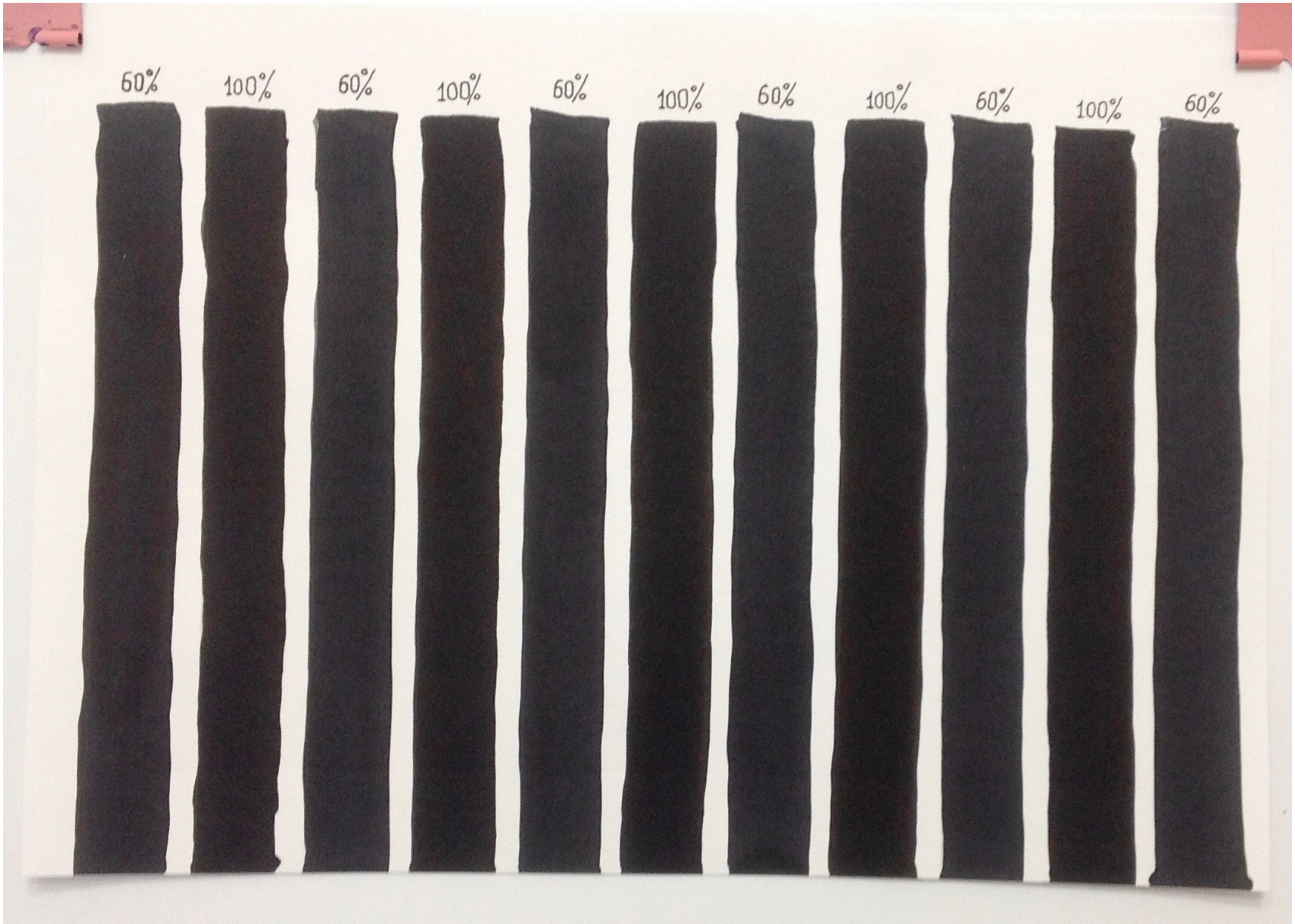

Figure 3. Stripes of as-purchased ink with no dilution (100%) and diluted to 60%.

Direction of view and direction of illumination are approximately normal to the surface of paper.

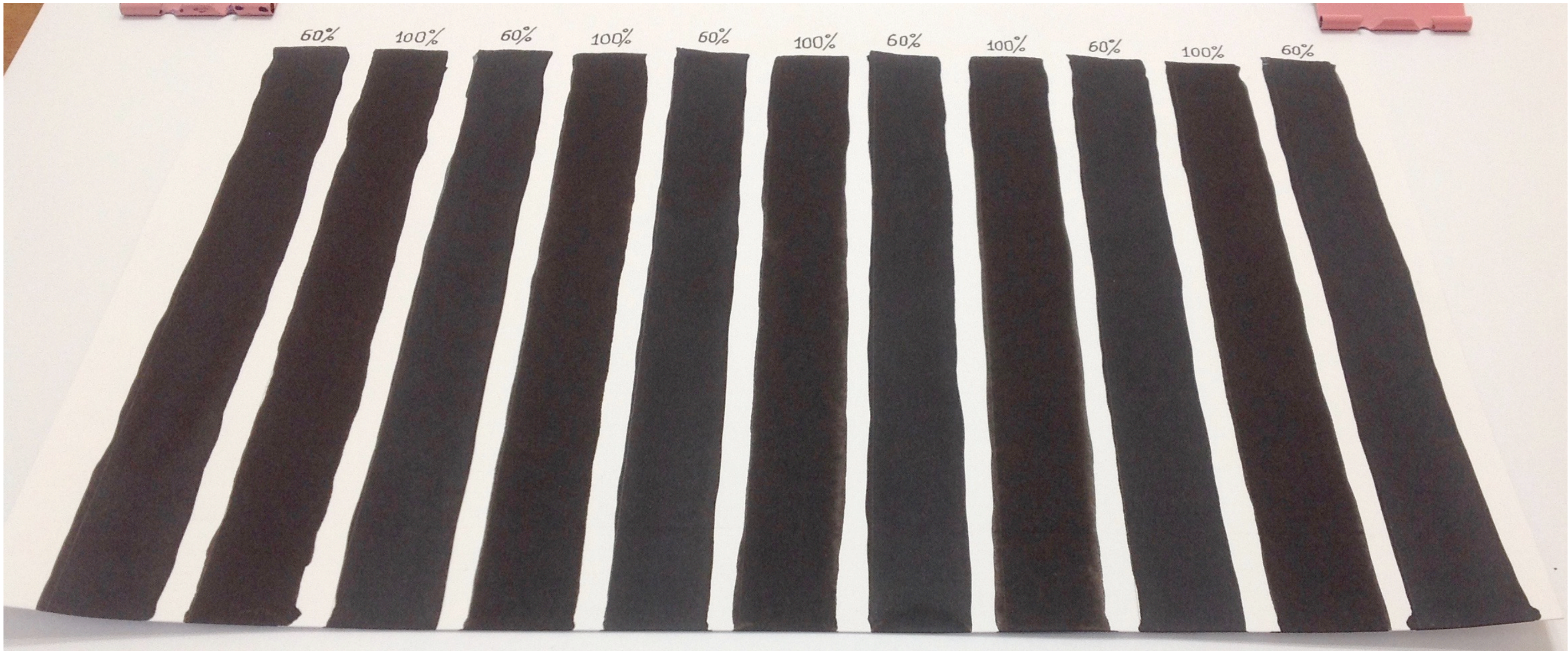

Figure 4. Stripes of as-purchased ink with no dilution (100%) and diluted to 60%.

Direction of view and direction of illumination are approximately at 45° to the surface of paper.

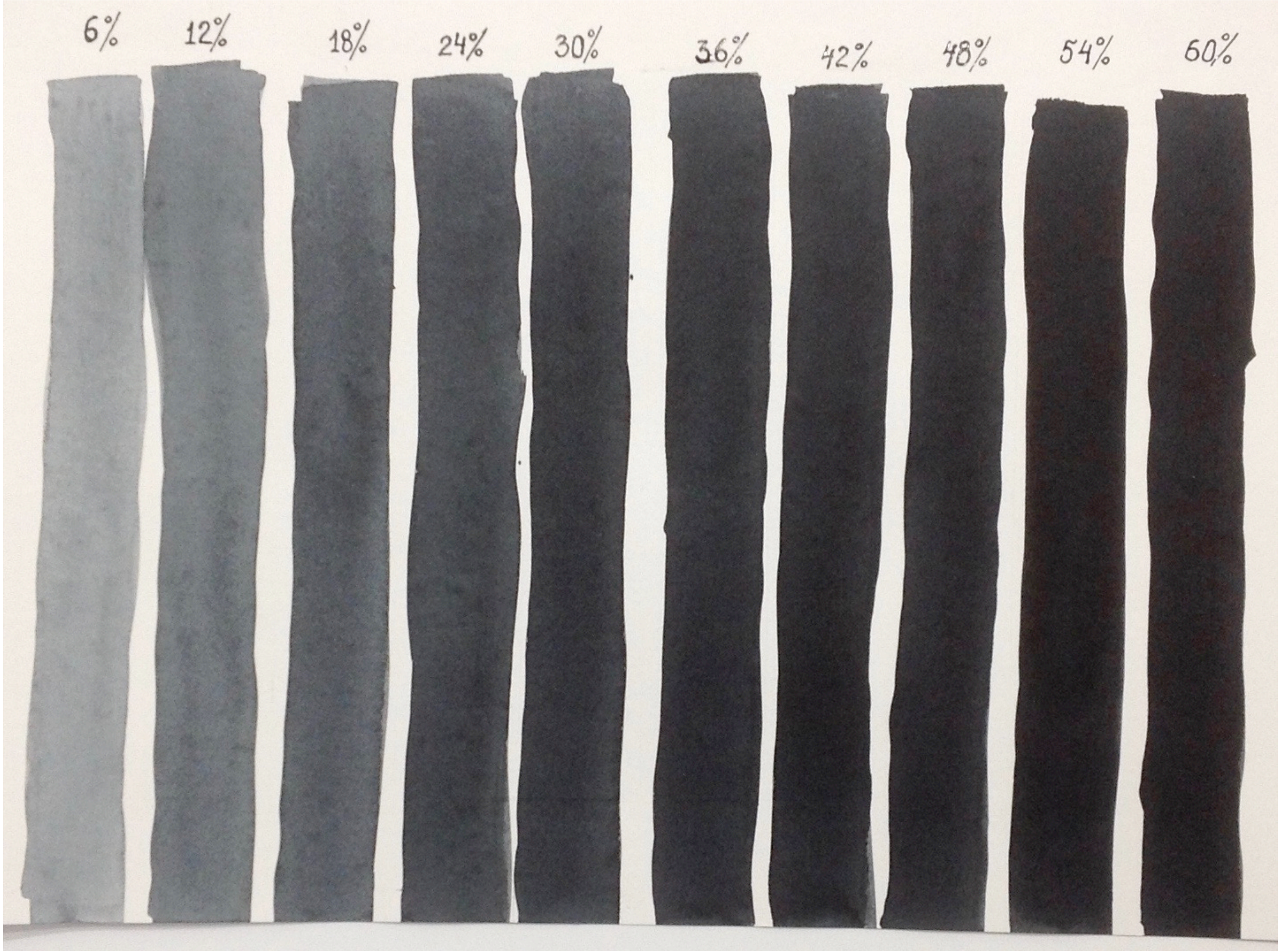

Figure 5. Stripes of as-purchased ink of different concentrations.

Concluding Remarks

(i) As a proof of concept, electrical conductance measurements were shown to be an effective and quite simple way in determining HWCP value for one brand of water-based ink.

(ii) It is clear that an approach disclosed here can be extended to any pigment-containing material.

(iii) Knowledge of HWCP value for any given material would allow one to run time/money saving intelligent testing of the material only at one single concentration of pigment, which is HWCP. Indeed, chart below (Chart 1) illustrates the basic idea of using HWCP value by manufacturer. Chart 2, on the other hand, depicts beneficial usage of DF value by artist.

(iv) Author hopes that the process of providing products with their DFs will become a *bona fide* practice and some sort of a quality marking among manufacturers. Moreover, supplying market with sample products at their HWCPs (*i.e*. DFs ≈ 0) would also be helpful and greatly appreciated by customers.

(v) HWCP will potentially be a keystone concept in solving a color-mixing problem in art and industry. It is well known that pigment mixing is a very capricious process at present. The procedure is mostly based on trial-and-error approach with no solid scientific foundation. In general, no one *a priori* knows what color he/she gets (*e.g.* RGB value) after mixing pigments at their arbitrary chosen ratio. The problem is especially acute for products with beneficially high DF values (*e.g.* products by *Daniel Smith*).

HWCP concept dictates a pigment color calibration procedure to be performed within linear regions, *i.e.* at pigment concentrations that are not exceeding their HWCPs. Proper color calibration of a few basic pigments (in progress) would allow one predictably construct any color he/she wants.

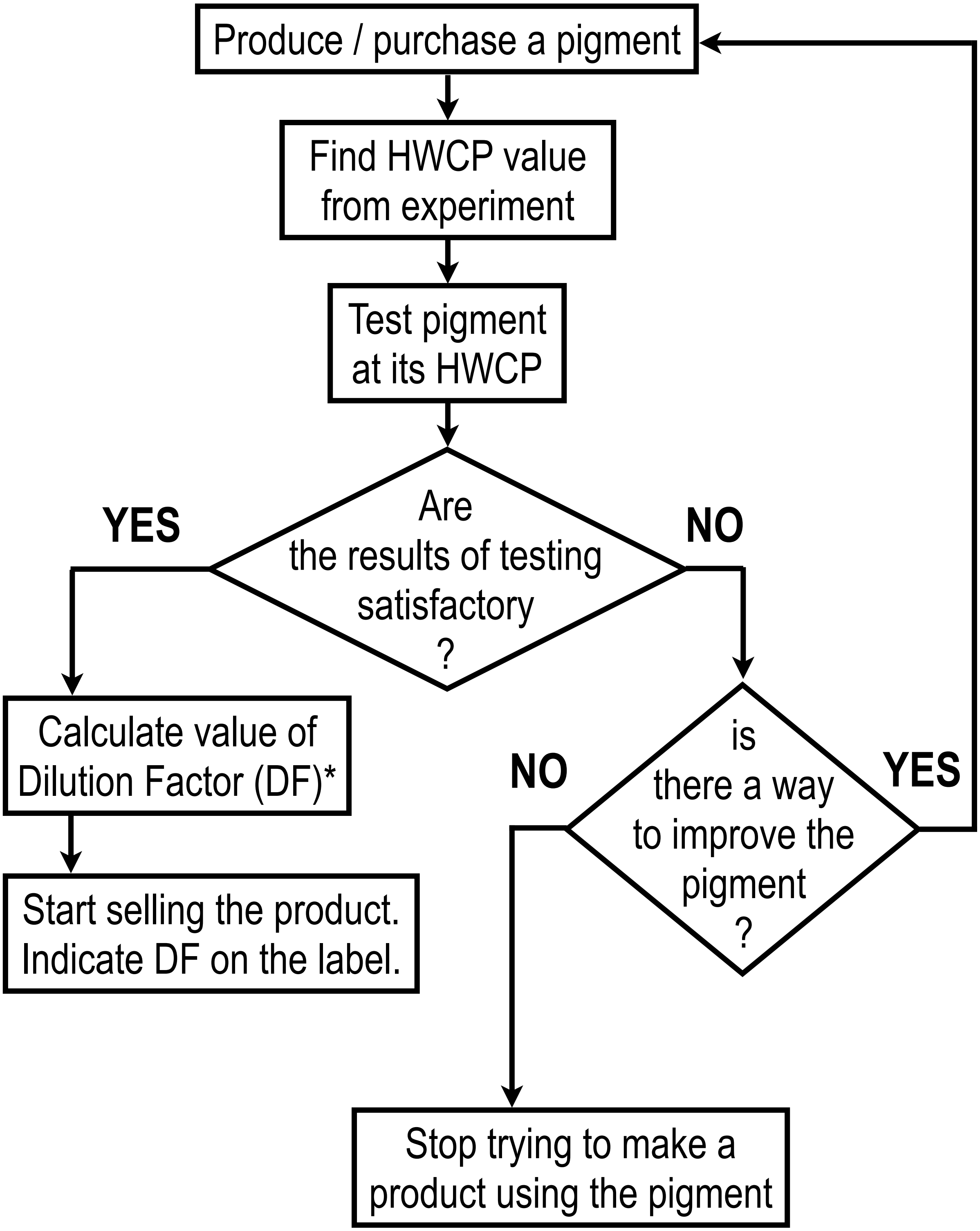

Chart 1. What–to-do chart for manufacturer.

* Dilution factor (DF) indicates how many parts of diluent per one part of the product should be taken in order to prepare working solution at HWCP.

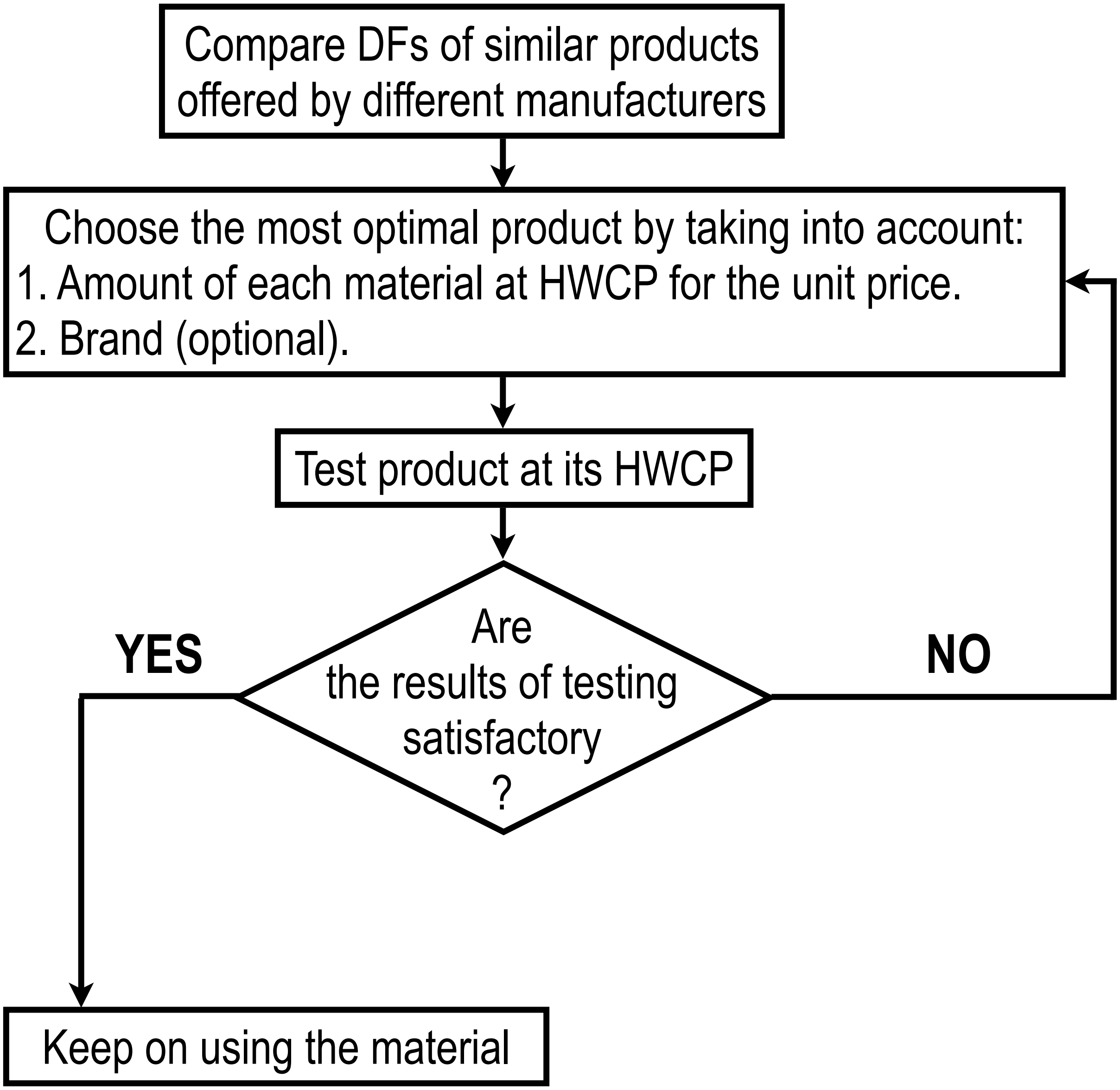

Chart 2. What–to-do chart for artist.

References

1. А.Я. Шаталов, И.К. Маршаков, *Практикум по физической химии*, Высшая Школа, 1968

2. *Rembrandt Drawings. 116 Masterpieces in Original Color*, Dover Publications, Inc., 2007

Supplementary Information

Materials

Black ink by *Gamma* (www.artgamma.ru) was used in experiments as a subject of study.

Commercially available distilled water by *Eltrans-Auto* (www.eltrans-auto.ru) was used to prepare working solutions from as-purchased ink.

Two 1 ml (± 0.025 ml) plastic syringes with scales were used to take aliquots of the liquids (distilled water; as-purchased ink, working solutions).

Preliminary water-treated, stretched, and dried paper *MixedMedia* by *Fabriano* was used as a substrate to test sample washes.

Resistors of following ratings were used in running procedure to correct readings of homemade ohmmeter: 3.9M; 1.2M; 910K; 820K; 680K; 510K; 430K; 330K; 240K; 150K; 110K; 91K; 82K; 75K; 62K; 51K; 39K; 30K; 20K; 10K; 7.5K; 6.2K; 5.1K; 3.9K; 3K; 2K; 1.5K; 1K; 820; 620; 470; 360; 300; 240; 200; 150; 100; 51; 47.

Instruments

Conventional resistance measurements were done using *Kaise KT-25* digital multimeter.

Homemade electrochemical cell (e.cell) with working electrodes made from diam. 1.5 mm stainless steel wire was used to contain working solutions and provide measurements of their resistances (Fig. 6).

Arduino-like *UNO* microcontroller was used as a platform for homemade ohmmeter to measure resistances of working solutions placed into e.cell (Fig. 7).

Readings were output onto the screen of *NOKIA 5110* LCD (Fig. 7).

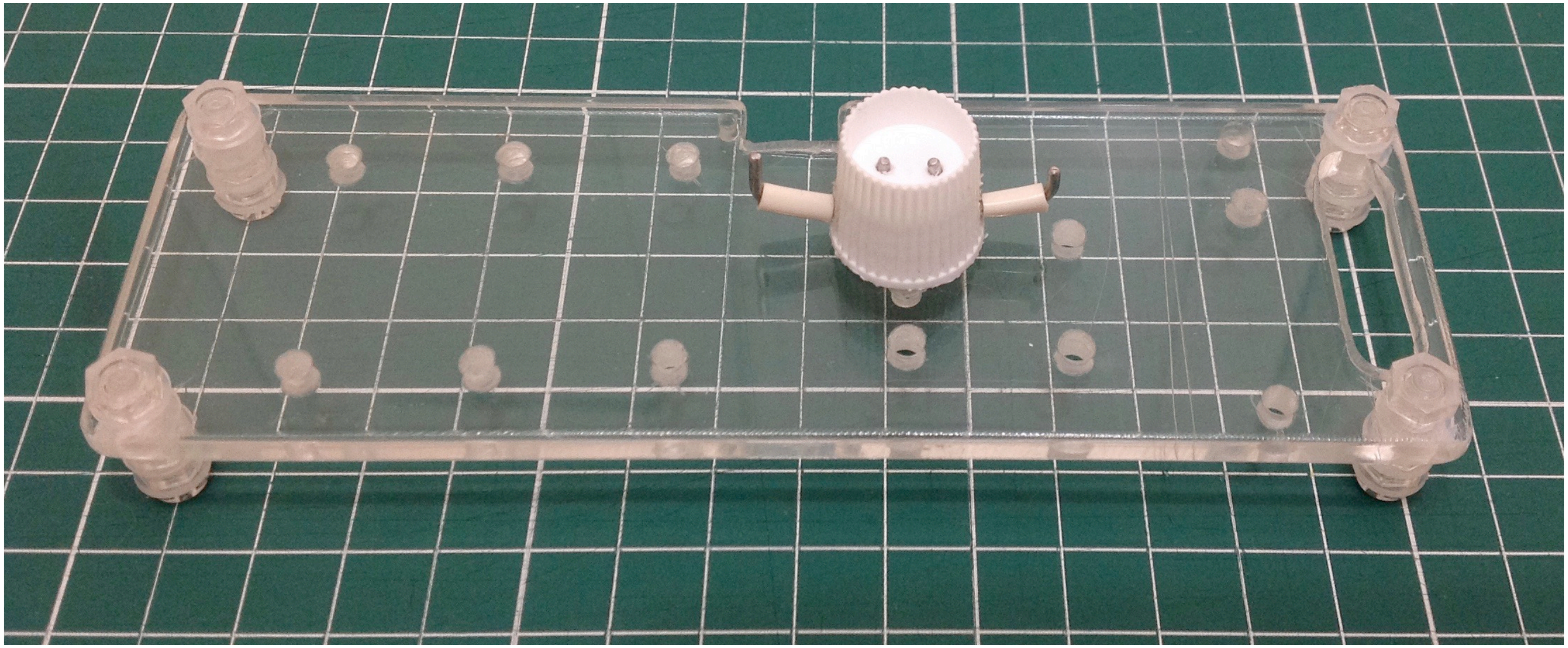

Figure 6. Homemade electrochemical cell mounted on the stand. Size of the grid 1 x 1 cm.

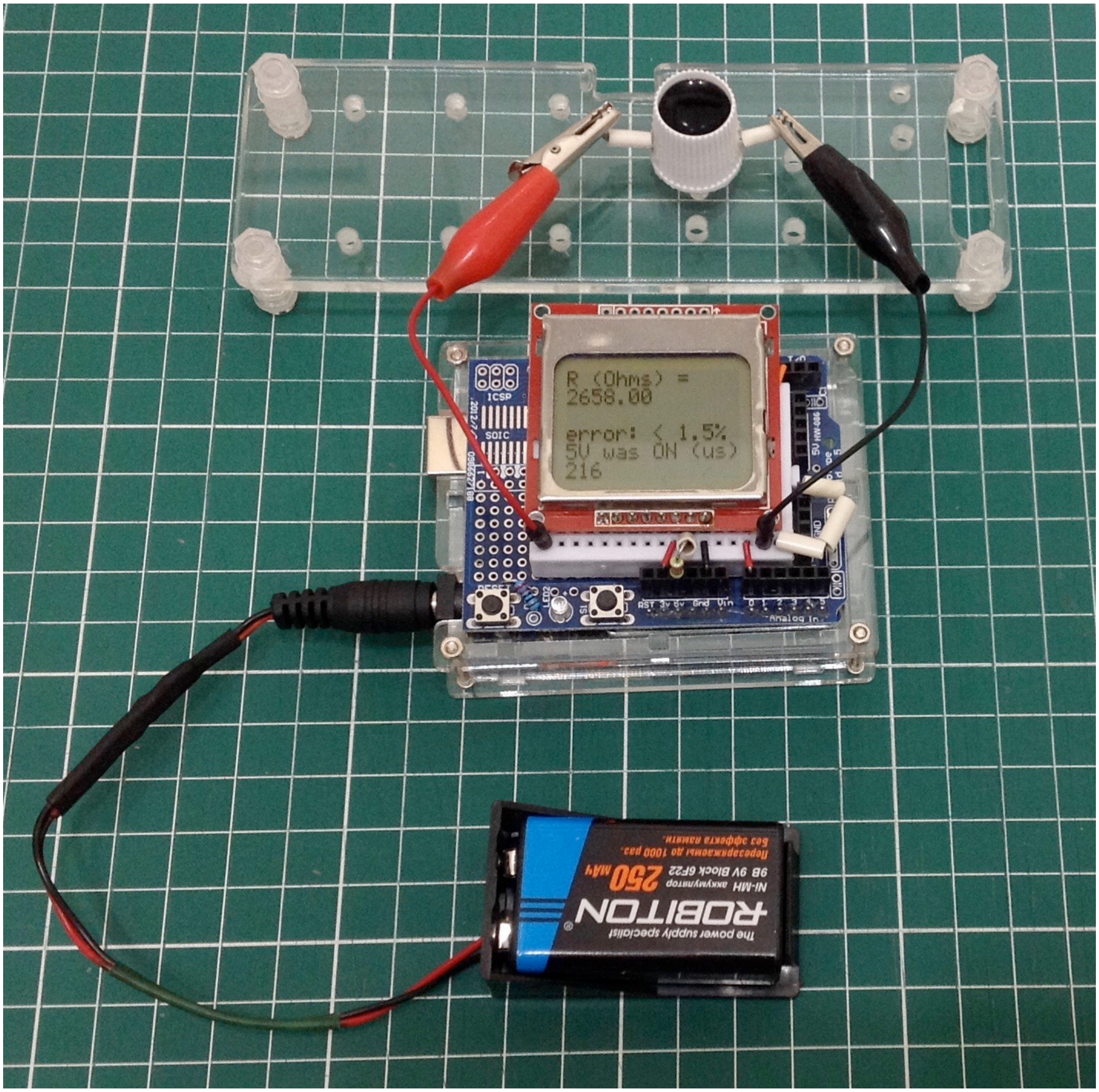

Figure 7. Hardware setup for conductivity measurements.

Measurements procedure

Each set of measurements followed the sequence: distilled water; as-purchased ink; aqueous solutions of ink with ever decreasing concentrations. Thus, data for conductance curve were collected in the direction from F – to D – to C (Fig.1). Each reading was considered as datum only after having getting the same reading in at least three consecutive measurements. Each measurement was initiated by pressing *reset* button (Fig. 7). Resistance data in ohms (*R*) were converted to conductance values in siemens (*S*) using $S = 1/R$ relation.

Homemade ohmmeter

To avoid polarization effects, resistances of the solutions are usually measured using AC of 50Hz - several kHz [1]. In this study, Arduino-like *UNO* microcontroller was used for its ability to perform sequence: *turn on 5V voltage between electrodes of e.cell → run a resistance measurement → turn the voltage off* for a very short period of time (216 μs) right after the *reset* button was pressed once. Time of 216 μs approximately corresponds to a half of period of 2 kHz AC.

Hardware schematic is below (Fig. 8).

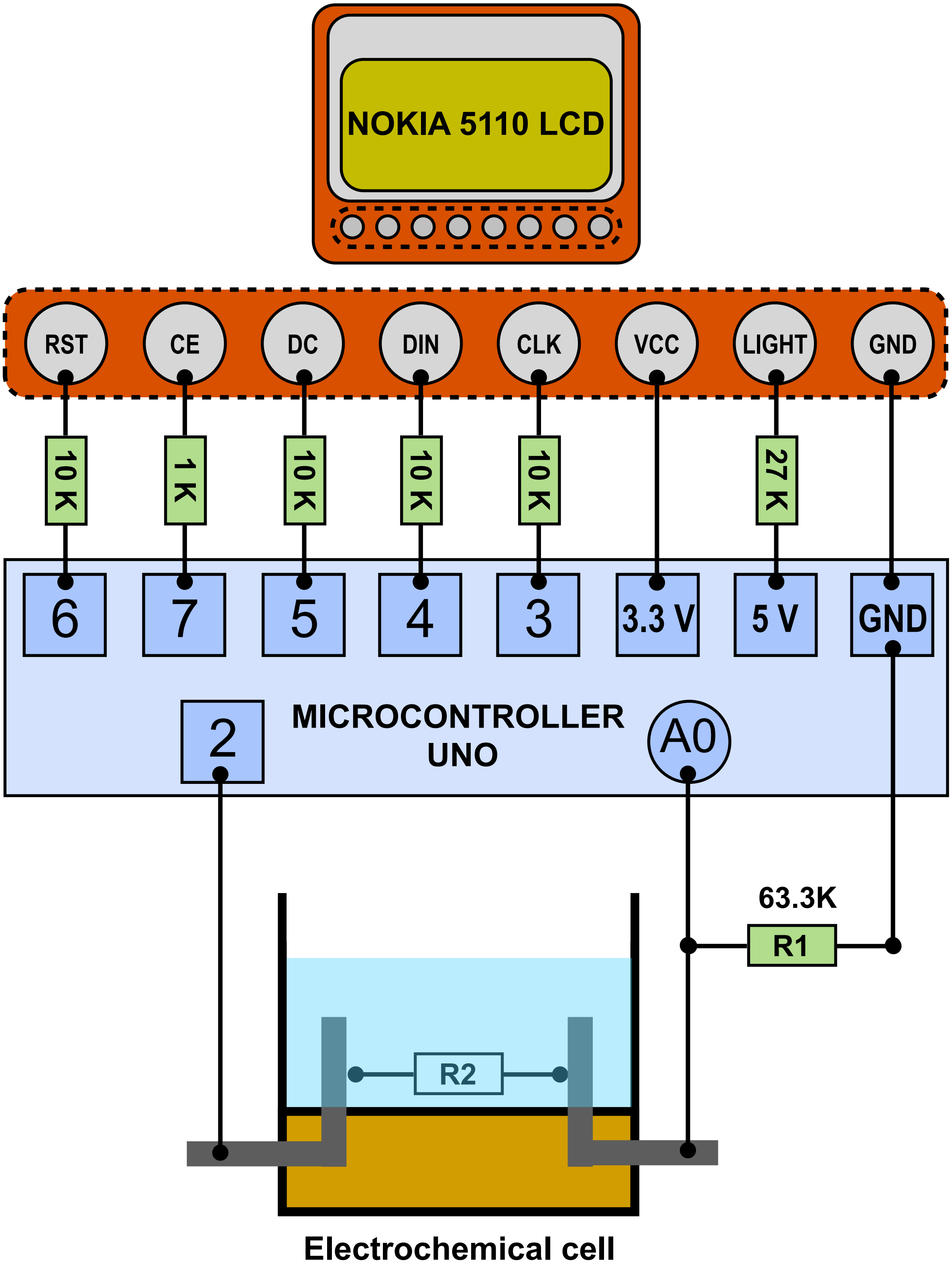

Figure 8. Hardware schematic.

Supplementary Information

To compensate distortions in reading resistances that values are much different from the reference *R1* value, two sets of measurements of standard resistors (see Materials) were done:

1st set – measurements are done using conventional multimeter;

2nd set – measurements are done using homemade ohmmeter.

The sets were mutually correlated with 4-term polynomial fit function then.

Coefficients of the fit function were implemented into the original code to correct raw readings. Final code is below.

```
/*  Arduino Ohmmeter to Nokia
The original sketches and schematics are taken from:
1. ISBN: 978-1-4493-6066-5;
2. https://create.arduino.cc/projecthub/muhammad-aqib/interfacing-nokia-
5110-lcd-with-arduino-7bfcdd
3. https://playground.arduino.cc/Learning/LEDSensor/
4. https://www.tutorialspoint.com/calculate-time-of-operation-in-arduino

The sketch supplies measurements of resistance and outputs data onto NOKIA
lcd along with the time the voltage was on.  Voltage is supplied to testing
resistance for a time of the measurements only.

The readings are corrected.

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v.8
*/  // set  up pins on Arduino
#define VOLTAGE 2 // defines digital pin D2 to supply 5V voltage for
measurements
int analogPin = A0; // reads the resistance of R2 via A0 pin
int raw = 0; // variable to store the raw input value
float R1 = 63300; // variable to store the R1 value which is 63.3K
float R2 = 0; // variable to store the R2 value
float buffer = 0; // buffer variable for calculation

float K0 = 10; // readings correction coefficient
float K1 = 1.0022; // readings correction coefficient
float K2 = -0.000000031166; // readings correction coefficient
float K3 = 0.000000000000000046416; // readings correction coefficient

float R2C = 0; // variable to store the corrected R2 value

// set up Nokia lcd
#include <PCD8544.h>
 PCD8544 lcd;

void setup() {
  lcd.begin(84, 48);
}

void loop()
```

```
{
  pinMode(VOLTAGE, OUTPUT); // prepares D2 pin for supplying 5V voltage

  long int t1 = micros(); // starts measuring time while voltage is ON
  digitalWrite(VOLTAGE, HIGH); // turning 5V voltage ON via pin D2

  raw = analogRead(analogPin); // reads the input pin

  digitalWrite(VOLTAGE, LOW); // turning 5V voltage OFF via pin D2
  long int t2 = micros(); // registers time the volage is turned OFF

  // raw readings resistance calculation
  buffer = 1023.00/raw;
  buffer = buffer-1;
  R2 = R1 * buffer;

  // readings correction
  buffer = R2 * R2;
  buffer = R2 * buffer;

  R2C = K3 * buffer;
  buffer = R2 * R2;

  buffer = K2 * buffer;

  R2C = R2C + buffer;

  buffer = K1 * R2;

  R2C = R2C + buffer;

  R2C = K0 + R2C;

  R2C = round(R2C); // rounding output data

  lcd.setCursor(0, 0);

  // checking if reading values are within the area of definition
  if (raw < 2) lcd.print("R > 16M"), delay(1000000000);
  if (raw > 1021) lcd.print("R < 150 Ohms"), delay(1000000000);

  lcd.print("R (Ohms) = ");

  lcd.setCursor(0, 1);
  lcd.print(R2C); // corrected resistance readings output

  lcd.setCursor(0, 4);
  lcd.print("5V was ON (us)");
  lcd.print(t2-t1);

  lcd.setCursor(0, 3);
  if (R2C >= 630) lcd.print("error: < 1.5%"), delay(1000000000);
  lcd.print("error: 6-8%");

  delay(1000000000);
}
```