

## Smartphone digital image colorimetry for the determination of aluminum in antiperspirant products

### Akıllı telefon dijital görüntü kolorimetresi ile terlemeyi önleyici ürünlerde alüminyumun belirlenmesi

Running title: SDIC of aluminum in antiperspirant products

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#### ABSTRACT

**Introduction:** The aim of this study is to present a method for the determination of the aluminum in antiperspirant products by chelating it with quercetin prior to its detection by smartphone digital image colorimetry (SDIC).

**Methods:** Samples were prepared by closed-vessel acid digestion in Teflon cups. This was followed by complexation of Aluminum in the sample solution using quercetin as chelating agent. Sample solutions were transferred to a quartz UV/Vis microcuvette for detection in a homemade colorimetric box designed for capturing images of the yellow complex with a smartphone camera. The pixel intensity of the images was converted to numbers for quantitation using ImageJ software for personal computer. An independent study using HPLC was carried out for checking the accuracy of the proposed method.

**Results:** Optimum SDIC conditions include Samsung C9 smartphone as detection camera, a cropped region of interest of  $6400\text{ px}^2$ , the side position of the colorimetric box was selected for capturing the images of the sample solutions placed 10 cm from the detection camera. Whereas optimum complexation conditions were found as sample pH of 5.5, sample volume of 3.0 mL, complexation time of 1.0 min and ligand concentration of  $0.28\text{ mmol L}^{-1}$ . Analytical performance of the method includes; limit of detection of  $0.5\text{ }\mu\text{mol L}^{-1}$  and coefficient of determination ( $R^2$ ) of the calibration graph was 0.9981.

**Discussion and conclusion:** The proposed method was successfully applied for the determination of aluminum in antiperspirant products with percentage recoveries ranging from 80.0 to 109.6%.

**Key words:** Aluminum; Antiperspirant products; Digital image colorimetry; Quercetin; Smartphone

## ÖZ

**Giriş ve amaç:** Bu çalışmanın amacı, kuersetin ile alüminyumun şelat oluşturması sonucu, akıllı telefon dijital görüntü kolorimetresi yöntemi ile terlemeyi önleyici ürünlerdeki alüminyum konsantrasyonunu belirlemektir.

**Yöntem ve gereçler:** Numuneler asit içinde özümsenerek kapalı teflon kaplarda hazırlanmıştır. Bunu, şelatlama maddesi olarak kuersetin kullanılarak numune solüsyonunda alüminyumun kompleksleştirilmesi izledi. Örnek çözeltiler, bir akıllı telefon kamerasıyla sarı kompleksin görüntülerini yakalamak için tasarlanmış ev yapımı bir kolorimetrik kutu içine yerleştirilmiş bir kuvars UV/Vis mikro küvetine aktarıldı. Görüntülerin piksel yoğunluğu, kişisel bilgisayar için ImageJ yazılımı kullanılarak miktar tayini için sayılarla dönüştürüldü. Önerilen yöntemin doğruluğunu kontrol etmek için HPLC kullanılarak bağımsız bir çalışma yapılmıştır.

**Bulgular:** Akıllı telefon dijital görüntü kolorimetresi optimum koşulları, algılama kamerası olarak Samsung C9 akıllı telefon,  $6400\text{ px}^2$  kırılmış bir ilgi alanı, algılama kamerasından 10 cm uzağa yerleştirilen örnek çözeltilerin görüntülerini yakalamak için kolorimetrik kutunun yan konumu seçilmiştir. Optimum kompleksleşme koşulları ise; numune pH'1 5.5, numune hacmi 3.0 mL, kompleksleşme süresi 1.0 dakika ve ligand konsantrasyonu  $0.28\text{ mmol L}^{-1}$  olarak bulunmuştur. Yöntemin analistik performansı ise şunları içerir;  $0.5\text{ }\mu\text{mol L}^{-1}$  saptama limiti ve kalibrasyon grafiğinin belirleme katsayıısı ( $R^2$ ) 0.9981'dir.

**Tartışma ve sonuç:** Önerilen yöntem, yüzde 80.0 ila 109.6 arasında değişen yüzde geri kazanımları ile terlemeyi önleyici ürünlerde alüminyum tayini için başarıyla uygulandı.

**Anahtar Kelimeler:** Alüminyum; Terlemeyi önleyici ürünler, Dijital görüntü kolorimetresi; Kuersetin; Akıllı telefon

## INTRODUCTION

Aluminum and its compounds are widely used in a variety of industries, including food, cosmetics, and pharmaceuticals.<sup>1</sup> Personal care products, such as deodorants and antiperspirant products (APPs), block body odor and reduce underarm sweat, they contain ingredients for pleasant odor, skin care and beauty.<sup>2</sup> The main active ingredients in APPs

are aluminum and zirconium compounds.<sup>3</sup> According to some studies, aluminum compounds can accumulate in the human body and are suspected of contributing to a variety of pathological disorders including anemia, bone disease, breast cancer, encephalopathy, Alzheimer's, Parkinson's, and other neurological disorders.<sup>4,5</sup> Despite the ongoing debate over the use of aluminum in APPs and the fact that the concentration of aluminum compounds on the final product is rarely reported, the number of analytical methods proposed for their determination in these samples remains very limited. Consequently, it is imperative to develop straightforward, rapid, and inexpensive analytical methods for this purpose in order to benefit consumers as well as governmental health agencies during the legislative process.

Although flame-atomic absorption spectrometry (FAAS) is the most commonly used technique for elemental determination, graphite furnace-atomic absorption spectrometry (GFAAS)<sup>6</sup> is preferred for aluminum, being a refractory element, due to the former's poor atomization efficiency and thus low sensitivity. Nonetheless, GFAAS is expensive, requires extensive experience to generate reproducible results, and is not available in many analytical laboratories. The techniques of choice for determining aluminum and its compounds in personal care products, including APPs, have been high-performance liquid chromatography with ultraviolet/visible detection (HPLC-UV/Vis),<sup>7,8</sup> flow injection-UV/Vis spectrophotometry,<sup>9</sup> and flow-through potentiometry.<sup>10</sup> Despite their numerous benefits, the high operating costs and high level of expertise required to use them make it hard for small laboratories to purchase and to use them efficiently. Furthermore, these instruments are electricity-dependent and not designed for on-field analysis, necessitating the development of alternative techniques. Miniaturized detection techniques that overcome these limitations have recently received special attention. A colorimetric solid-phase extraction method was proposed for the determination of aluminum, in which a membrane disk loaded with the colorimetric reagent pyridoxal salicyloylhydrazone allowed the extraction of the metal complex prior to its detection using a miniature fiber optic spectrometer.<sup>11</sup> To detect the aluminum complex in the visible region, a paper platform with alizarin S as a chromogenic reagent in a spot test was used in conjunction with diffuse reflectance spectroscopy using a portable spectrophotometer.<sup>12</sup>

Digital image colorimetry (DIC) is a new colorimetric technique that analyzes the basic red-green-blue (RGB) channels of images of a colored analyte solution captured by a digital camera, webcam, hand scanner, or smartphone camera.<sup>13,14</sup> Smartphones are regarded as the best image acquisition tools for this purpose due to their superior photography functions, software, and portability for image processing. Smartphone digital image colorimetry (SDIC) has been applied for the determination of total iron,<sup>15</sup> iron(II),<sup>16</sup> chromium(VI),<sup>17</sup> arsenic(III),<sup>18</sup> cobalt(II)<sup>19</sup> and boron<sup>20</sup> in addition to several organic analytes in a variety of samples. To the best of our knowledge, this is the first study on the use of SDIC for the determination of aluminum.

In this study, an SDIC method is proposed for the determination of aluminum in APP samples after chelating it with quercetin to form a yellow complex that can be easily

detected by a smartphone camera. The results of SDIC were compared with an HPLC with diode-array detection (DAD) method for accuracy check.

## MATERIALS AND METHODS

### Chemicals and reagents

All the reagents used were of analytical grade unless otherwise indicated. Acetic acid, HPLC-grade acetonitrile, aluminum nitrate nonahydrate, disodium phosphate, ethanol, hydrochloric acid, monosodium phosphate, nitric acid, quercetin and sodium acetate were from Sigma-Aldrich (Steinheim, Germany) while trifluoroacetic acid was from Fluka (Buchs, Germany). Deionized (DI) water ( $18.2\text{ M}\Omega\text{-cm}$ ), purified with Pure Lab Ultra Analytic (ELGA LabWater, High Wycombe, UK), was used for the preparation of all aqueous solutions.

### Instrumentation

A homemade colorimetric box with the dimensions of  $20 \times 15 \times 8\text{ cm}^3$  was used. The white interior walls provided uniform illumination. Sample solutions were transferred into a quartz UV/Vis microcuvette (Hellma, Kruibeke, Belgium) and placed inside the box 10.0 cm from the detection camera and 11.0 cm from a 1.2V/1300 mA battery-powered white light-emitting diode (LED) that illuminated the sample solution. Images were captured with the flash turned off. A schematic diagram of the colorimetric box is shown in Figure 1. Digital images were captured using an SM-C9 smartphone, equipped with a 16 MP rear camera with a resolution of  $4608 \times 3456$  pixels. Images were processed using the freely downloadable software ImageJ (PC version, 1.52a, Java 1.8.0\_212, 64 bit) from the National Institutes of Health, USA.<sup>21</sup> An HPLC instrument (1200 Series, Agilent Technologies, Santa Clara, CA, USA), equipped with a degasser, a quaternary pump, an autosampler, a column thermal jacket and DAD was used for accuracy check of the method.

### Standard solutions of aluminum

A  $3.7\text{ mmol L}^{-1}$  stock solution of aluminum was prepared by dissolving an appropriate mass of aluminum nitrate nonahydrate in  $0.10\text{ mol L}^{-1}$  hydrochloric acid solution, from which a  $0.37\text{ mmol L}^{-1}$  intermediate standard solution was prepared in the same diluent. Working standard solutions were prepared in the ranges of  $1.7\text{--}25.0\text{ }\mu\text{mol L}^{-1}$  for SDIC and  $3.3\text{--}60\text{ }\mu\text{mol L}^{-1}$  for HPLC-DAD in the same diluent. A  $3.3\text{ mmol L}^{-1}$  stock solution of quercetin was prepared by dissolving an appropriate mass of the solid in ethanol/DI water (60/40%, v/v). pH was adjusted to 5.5 with a  $1.0\text{ mol L}^{-1}$  acetate buffer solution.

## **Sample preparation**

Five APP samples of various brands were obtained from a local grocery and pharmacies in Nicosia, TRNC. The samples were digested using a previously developed method<sup>22</sup> with some modifications. Briefly,  $0.25\pm0.01$  g of each sample was weighed and digested in 3.0 mL of aqua regia in Teflon cups for 2 h at 100 °C in a closed-vessel digestion block. After allowing the samples to cool down to room temperature, they were filtered through a 0.22 µm Whatman filter paper into a 25.0 mL volumetric flask and the volume was completed to the mark with DI water. From this solution, 1.0 mL was transferred into another 25.0 mL volumetric flask and the volume was made up to the mark with DI. This solution will be referred to as the sample solution henceforth.

## **Complexation reaction and smartphone digital image colorimetry**

For complexation, 250 µL of the 3.3 mmol L<sup>-1</sup> quercetin solution were added to 50.0 µL of the sample solution in a 15 mL screw capped graduated polypropylene centrifuge tube. The mixture was made up to 3.0 mL with the pH 5.5 acetate buffer solution. After the solution was vortexed for 1.0 min, a portion (ca. 100 µL) was transferred into a quartz UV/Vis cuvette for SDIC analysis.

## **Data processing and statistical analysis**

Upon splitting the images into their RGB channels, the mean histogram values from the B channel were used for calibration and quantitation throughout the analysis. For statistical analysis, a single-factor analysis of variance test (ANOVA) in Microsoft Office Excel (2013 Windows, Microsoft Corporation, WA, USA) was used, with a P value less than 0.05 was considered to be statistically significant.

## **Chromatographic conditions**

The aluminum-quercetin complex and the excess ligand were separated using a reversed-phase column (Agilent Eclipse XDB-C18. 4.6 mm ID × 150 mm, 5 µm, Agilent Technologies, Santa Clara, CA, USA), a gradient elution consisting of 0.5% trifluoroacetic acid in DI water, pH 1.4 (solvent A) and acetonitrile (solvent B), with a gradient program of 10% solvent B at 0 min to 80% solvent B within 10 min at a flow rate of 1.0 mL min<sup>-1</sup>. Separation temperature and the injection volume were set at 30 °C and 20 µL, respectively. The maximum absorption wavelengths of the complex and ligand were 415 and 374 nm, respectively. The chromatograms obtained are given in Figure S1 (Supplementary Material).

## **RESULTS AND DISCUSSION**

### **Optimization of smartphone digital image colorimetry conditions**

## Data processing

The mean value of each channel was obtained from its histogram and the B channel, giving the highest intensity, was used for the rest of the experiments. Because in the RGB model, the more intense the color, the lower the values within the range of 0-255, the value obtained from the histogram required additional processing to obtain a positive slope. Beer's Law, represented by the equation  $R = \log(I_0/I)$ , where  $R$  is the response,  $I_0$  is the mean intensity of the blank, and  $I$  is the mean intensity of the analyte, all measured from the same channel, has been used to process RGB data in the literature.<sup>23</sup> The equations  $R = 255 - I$ ,<sup>24</sup> and  $R = I_0 - I_b$  were also used, where,  $I_0$  and  $I_b$  are the mean intensity of the blank and the analyte solutions in the blue channel, respectively.<sup>25</sup> In the present study, the data was processed using Equation 1.

$$R_B = 255 - I_B \quad \text{Equation 1}$$

where,  $R_B$  and  $I_B$  are the response and intensity of the analyte solution in the B channel, respectively.

## Detection camera and region of interest

The overall quality of an image is influenced by several factors, such as resolution, aperture, specifications of the light sensor as well as the algorithm applied for image processing.<sup>26</sup> The effect of camera type on the response was assessed using four different phones, namely SM-C9, Techno p-3, SM-S7 and iPad 1460 with camera resolutions of 16 MP, 13 MP, 12 MP, 5 MP, respectively. The response increased as the resolution increases (Figure 2, a), indicating that this parameter is important in determining the image quality. Therefore, SM-C9 was used for further analysis. The digital images captured for sample solutions were processed within a defined region of interest, with the area ranging from 400 to 14400 px<sup>2</sup>. The results revealed no significant differences in the response, owing primarily to the homogeneity of the sample solutions (Figure 2, b). An area of 6400 px<sup>2</sup> was used throughout the analysis.

## Position of camera and cuvette

When compared to the side position, the top position produced blurred images and a slightly lower response (Figure 2, c). As a result, the side position was used for further analysis. The effect of the distance between the sample solution and the detection camera was investigated over a range of 8.0-12.0 cm, with the image blurring below 8.0 cm. The response remained nearly constant throughout the studied range (Figure 2, d), indicating that the detection camera's maximum autofocus efficiency was achieved within this distance. For the following experiments, an optimal distance of 10.0 cm was chosen between the detection camera and the sample solution.

## Optimization of complexation conditions

## **Sample pH**

pH of the sample solution affects both the formation of a stable complex and the form of the analyte prior to complexation. Aluminum exists primarily in its trivalent form under acidic conditions, whereas increasing the pH leads to the formation of insoluble aluminum hydroxide at neutral pH.<sup>8</sup> The effect of pH on the analytical response was studied over a pH range of 4.5 to 6.5. The solution was colorless at pH less than 4.0 and an unstable yellow color formed at pH greater than 7.5. The response improved up to pH 5.5, beyond which, it declined and remained almost constant (Figure 3, a). A similar result was obtained in a previous study for the complexation pH of aluminum with quercetin.<sup>8</sup> As a result, pH 5.5 was deemed optimal throughout the study.

## **Concentration of the ligand**

To ensure that the maximum yield of the complexation reaction was achieved, the addition of an excess amount of quercetin is necessary. The effect of the ligand concentration was carried out by using a fixed concentration of aluminum ( $0.31 \text{ mmol L}^{-1}$ ), in a 3.0 mL sample solution buffered at pH 5.5, and varying the concentration of quercetin from 0.06 to  $0.50 \text{ mmol L}^{-1}$ . The response increased with increase in the concentration of quercetin up to  $0.28 \text{ mmol L}^{-1}$ , after which it remained constant, indicating that the optimum molar ratio of metal to ligand was reached, which was in accordance with the theoretical stoichiometric mole ratio of 1:1 between aluminum and quercetin, as also found experimentally in a previous study.<sup>7</sup> Therefore, the optimum concentration of quercetin was taken as  $0.28 \text{ mmol L}^{-1}$  (Figure 3, b).

## **Sample volume and complexation time**

The sample volume affects the concentration of the aluminum-quercetin complex in the final solution. The effect of increasing the sample volume was investigated from 3.0 to 7.0 mL. It is noteworthy that 3.0 mL was the minimum sample volume suitable to obtain a buffered solution after acid digestion of the real samples. Expectedly, the response decreased with an increase in the volume of the sample solution due to dilution of the metal complex in the final solution (Figure 3, c). As a result, the optimum sample volume was selected as 3.0 mL. The time interval between adding the ligand to the sample solution and detecting the yellow complex was defined as the complexation time, which corresponded to the vortex mixing period. The effect of complexation time was studied over the range of 1.0-5.0 min. The addition of the ligand resulted in instantaneous formation of a stable complex, as indicated by its consistent yellow color. (Figure 3, d). Therefore, an optimum complexation time was selected as 1.0 min to ensure a good repeatability.

## **Analytical performance**

An aqueous calibration curve was plotted using standard aluminum solutions at concentrations ranging from  $1.7$  to  $25.0 \mu\text{mol L}^{-1}$  to assess the analytical performance of the proposed method. A linear calibration graph was obtained with a coefficient of

determination ( $R^2$ ) of 0.9981 (Table 1). Repeatability was evaluated in terms of intraday and interday precision. The results, expressed as percentage relative standard deviation (%RSD) were less than 2.2% and 3.1%, respectively. The limit of detection (LOD), calculated based on  $3S_b/m$ , where  $S_b$  is the standard deviation of the intercept and  $m$  is the slope of the regression equation, was found as  $0.5 \mu\text{mol L}^{-1}$  ( $0.2 \mu\text{g g}^{-1}$ ) and the limit of quantitation (LOQ), based on  $10S_b/m$ , was found to be  $1.7 \mu\text{mol L}^{-1}$  ( $0.7 \mu\text{g g}^{-1}$ ).

### Determination of aluminum in antiperspirant products

All five of the analyzed samples were found to contain aluminum at concentrations in the range of 2.4 to 3.5% (w/w) (Table 2). Accuracy of SDIC was checked using an addition-recovery test by spiking the samples with aluminum (as aluminum nitrate nonahydrate to the genuine sample) at three concentration levels (i.e., 1.0, 3.0 and 5.0 %w/w). The percentage absolute recoveries (%R), calculated from the aqueous calibration curve, were found to range between 80.0 and 109.7 (Table 2). An independent HPLC study found no statistically significant difference between the results obtained with both techniques ( $P > 0.05$ ) for all samples (Table 2), indicating good accuracy of the proposed SDIC method.

### Comparison with other methods

The proposed SDIC method was compared with the HPLC-DAD method in terms of linearity, sensitivity, linear dynamic range, precision, analysis time and organic solvents consumption (Table 1 and Table 3). The main advantages of SDIC over HPLC-DAD are the significantly lower cost of purchase, operation and maintenance as well as the shorter analysis time, i.e., 1 versus 8 min, respectively (Table 3). Likewise, the proposed method was compared to other methods used for the determination of aluminum in personal care products. The results, summarized in Table 3, reveal that the proposed method is superior to the others in terms of cost, degree of greenness and ease of implementation. Furthermore, it outperformed the others due to its zero organic solvent consumption, one-minute analysis time and low energy dependence. Despite the fact that PPC-DRS did not require any organic solvents, the analysis time was rather long.<sup>12</sup> The analysis time in FTPS was only 0.5 min, but it required 3 mL of organic solvents per sample.<sup>10</sup> SDIC was more sensitive than the other methods except for DLLME-UV/Vis<sup>27</sup> but the analysis time was longer.

## CONCLUSION

In this study, smartphone digital image colorimetry (SDIC) was developed for the determination of aluminum in antiperspirant products. Quercetin was used as a ligand to form an easily detectable yellow complex with aluminum. The proposed method could be used to accurately determine aluminum in genuine samples as demonstrated by high-performance liquid chromatography-diode array detection (HPLC-DAD) and addition-recovery tests. In comparison to the latter method and others used in the literature for determining aluminum in personal care products, including antiperspirant, the proposed method offers several significant advantages, including low operation and maintenance

costs, short analysis time, high degree of greenness, simplicity of execution, zero organic solvent consumption, minimal energy dependency, portability and high potential for on-field analysis. The obtained results show that SDIC is a viable alternative to sophisticated instrumental techniques that are not easily owned and/or operated by every laboratory for the determination of inorganic and organic analytes in a wide range of samples.

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## **DISCLOSURE STATEMENT**

No potential conflict of interest was reported by the author(s).

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## TABLES

**Table 1.** Comparison of the analytical figures of merit of the proposed smartphone-digital image colorimetry method with high-performance liquid chromatography-diode array detection for the determination of aluminum in antiperspirant products.

Analytical Technique	Regression equation <sup>a</sup>	$R^{2b}$	LOD <sup>c</sup>	LOQ <sup>d</sup>	LDR <sup>e</sup>	%RSD <sup>f</sup>	
						Intraday	Intraday

HPLC-DAD	$Y = 1.38(\pm 0.02)x + 0.93(\pm 0.45)$	0.9993	1.0 (0.3 μg g⁻¹)	3.3 (1.1 μg g⁻¹)	3.3-60.0	2.3	3.0
SDIC	$Y = 2.36(\pm 0.03)x - 0.0016(\pm 0.40)$	0.9981	0.5 (0.2 μg g⁻¹)	1.7 (0.7 μg g⁻¹)	1.7-25.0	2.2	3.1

<sup>a</sup>Response = Slope (±SD) × [Aluminum concentration (μmol L⁻¹)] + Intercept (±SD).

<sup>b</sup>Coefficient of determination.

<sup>c</sup>Limit of detection (μmol L⁻¹).

<sup>d</sup>Limit of quantitation (μmol L⁻¹).

<sup>e</sup>Linear dynamic range (μmol L⁻¹).

<sup>f</sup>Percentage relative standard deviation,  $n = 3$ .

**Table 2.** Percentage recoveries of aluminum from antiperspirant products using smartphone-digital image colorimetry and high-performance liquid chromatography-diode array detection obtained with standard-addition and recovery tests.

Sample <sup>a</sup>	Added (%, w/w)	Found (SDIC) (%, w/w)	%R <sup>b</sup>	Found (HPLC-DAD) (%, w/w)
APP1	-	2.9 (±0.2)	-	3.2 (±0.2)
	1.0	4.0	105.0	
	3.0	5.8	95.0	
	5.0	7.5	90.2	
APP2	-	2.4 (±0.9)	-	3.3 (±0.2)
	1.0	3.2	80.0	
	3.0	5.6	109.7	
	5.0	7.2	97.2	
APP3	-	2.7 (±0.4)	-	3.2 (±0.2)
	1.0	3.6	85.0	
	3.0	5.7	99.0	
	5.0	8.1	107.2	
APP4	-	2.6 (±0.3)	-	2.4 (±0.1)
	1.0	3.5	89.0	
	3.0	5.8	105.0	
	5.0	8.0	107.8	
APP5	-	3.3 (±0.2)	-	3.5 (±0.1)
	1.0	4.3	100.0	
	3.0	6.2	96.0	
	5.0	7.8	90.2	

<sup>a</sup>APP: Antiperspirant product.

<sup>b</sup>Percentage recovery, a value obtained considering extraction yields from aqueous calibration graph.

**Table 3.** Comparison of smartphone digital image colorimetry with other methods for the determination of aluminum in different types of samples.

Method <sup>a</sup>	Sample	Analysis time (min)	V <sub>org.</sub> <sup>b</sup> (mL)	LOD <sup>c</sup> ( $\mu\text{g mL}^{-1}$ )	R <sup>d</sup>	%RSD <sup>e</sup>	Ref.
CSPE-DRS	Cookware, antacids, hygienic care products	67	159	0.18	0.992	8.8	[11]
LLE-HPLC-UV/Vis	Antiperspirants	46	12.5	1.24	0.997	5.5	[8]
FI-UV/Vis	Antiperspirants	44	60	0.0161	0.9992	< 2	[9]
DLLME UV/Vis	Water, Food, biological, pharmaceuticals	32	0.2	0.0002	0.9975	1.8-3.3	[27]
PPC-DRS	Antiperspirants	12	0	3.06	0.999	< 5.0	[12]
FTPS	Deodorants	0.5	3	0.5	0.994	3	[10]
HPLC-DAD	Antiperspirants	8	0	0.027	0.9993	3.0	This study
SDIC		1	0	0.013	0.9981	3.1	

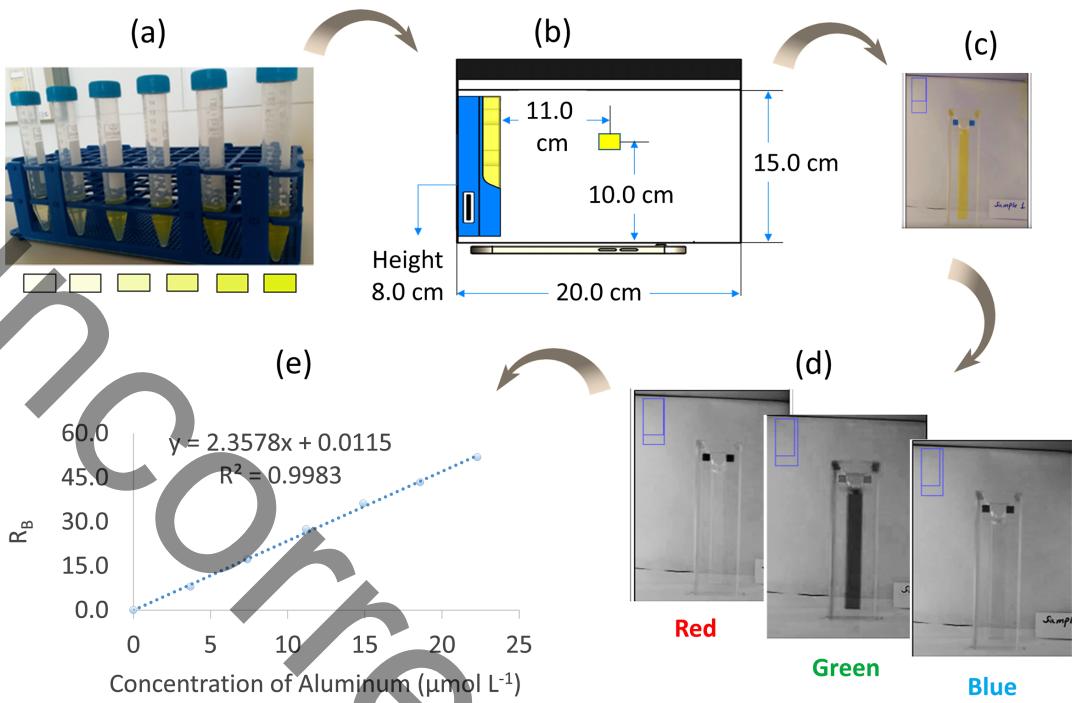
<sup>a</sup>CSPE-DRS: Coupled colorimetric solid-phase extraction-diffusive reflectance spectroscopy; LLE-HPLC: Liquid-liquid extraction-high performance liquid chromatography; FI-UV/Vis: Flow injection-ultraviolet/visible spectrophotometry; DLLME-UV/Vis: Dispersive liquid-liquid microextraction-ultraviolet/visible spectrophotometry; PPC-DRS: Paper platform for colorimetric determination-diffuse reflectance spectroscopy; FTPS: Flow-through potentiometric sensors; HPLC-DAD: High-performance liquid chromatography-diode array detector; SDIC: Smartphone digital image colorimetry.

<sup>b</sup>Volume of organic solvents consumed.

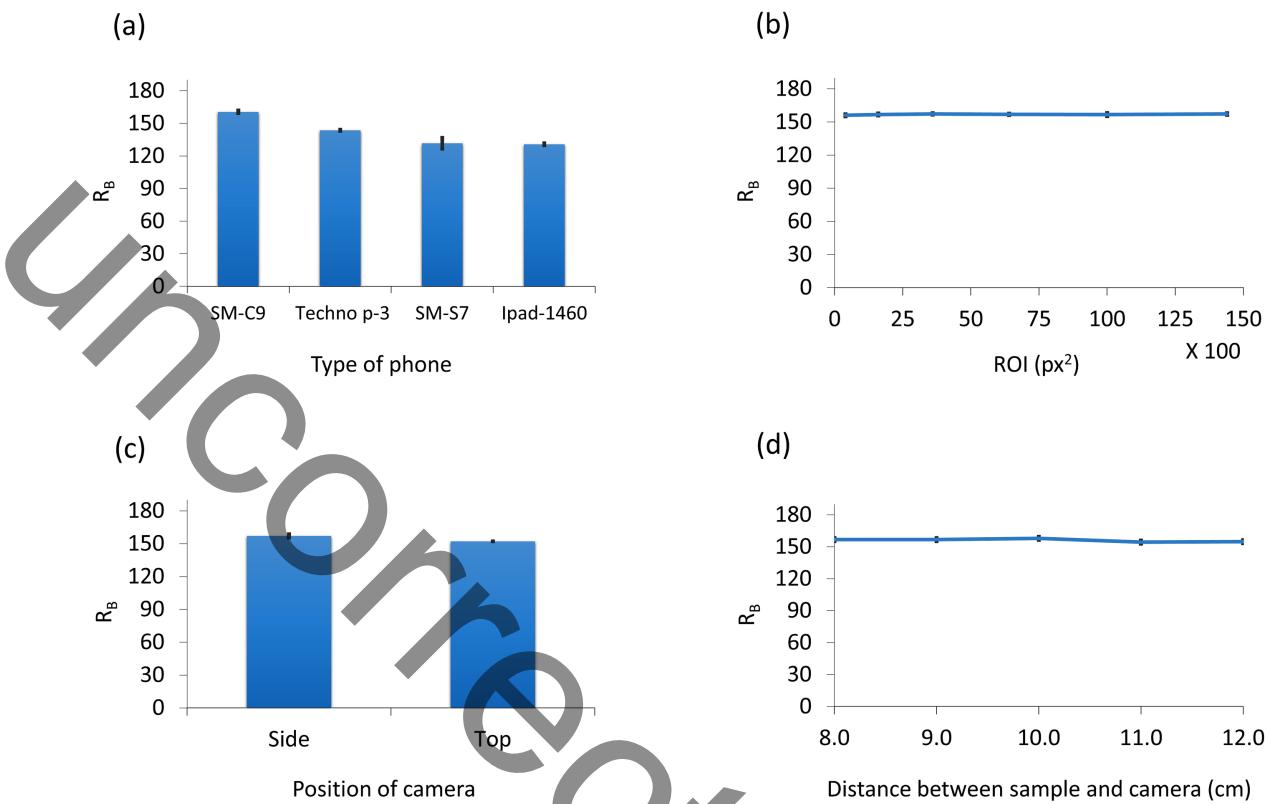
<sup>c</sup>Limit of detection.

<sup>d</sup>Coefficient of determination.

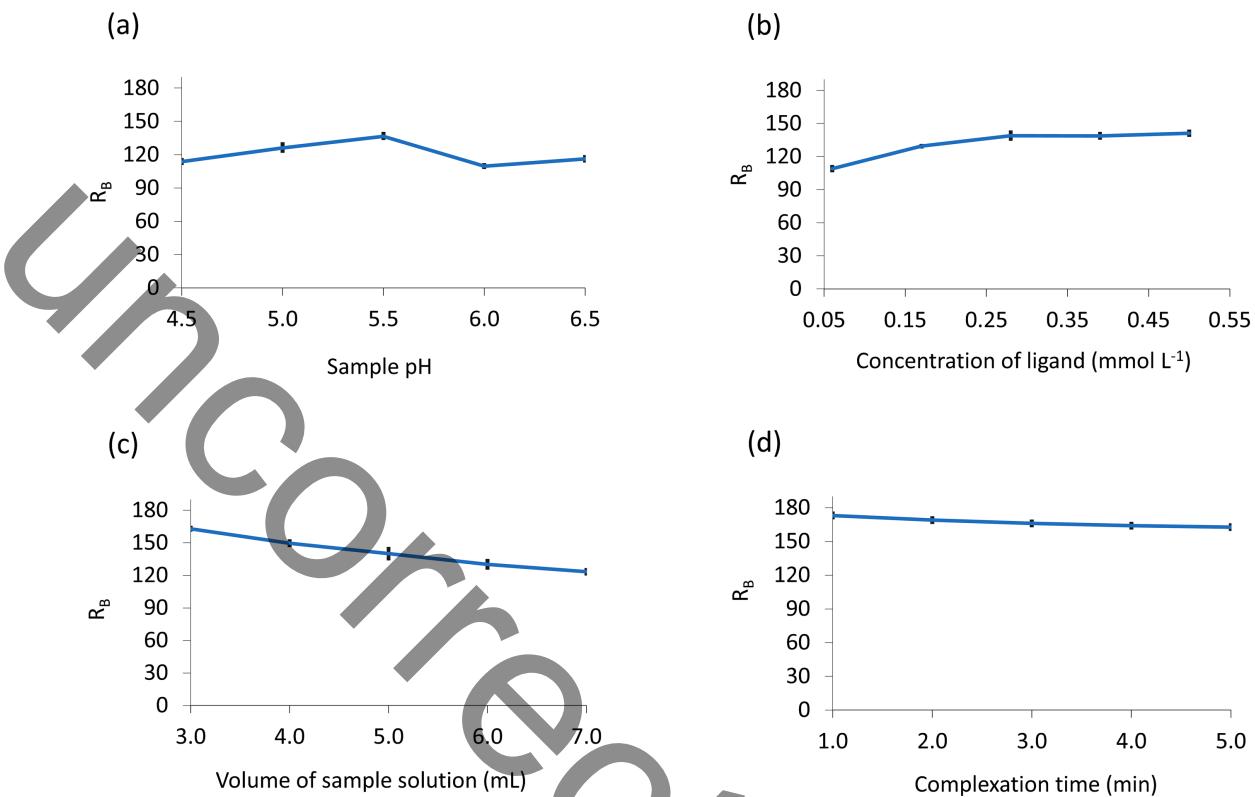
<sup>e</sup>Percentage relative standard deviation.



**Figure 1.** Proposed smartphone digital image colorimetry system: (a) Solution of aluminum-quercetin complex at different concentrations; (b) Colorimetric box; (c) Image of sample; (d) Image split into red-green-blue channels; (e) Histogram of the blue channel; and (f) External aqueous calibration graph;  $R_B = 255 - I_B$ , where,  $R_B$  and  $I_B$  are the response and intensity of the analyte solution in the B channel, respectively.



**Figure 2.** Optimization of smartphone digital image colorimetry parameters: (a) Type of phone; (b) Area of region of interest; (c) Position of camera; (d) and Distance between sample and camera. Optimum complexation conditions: Sample pH, 5.5; concentration of ligand, 0.28 mmol L<sup>-1</sup>; volume of sample solution, 3.0 mL; and complexation time, 1.0 min;  $R_B = 255 - I_B$ , where,  $R_B$  and  $I_B$  are the response and intensity of the analyte solution in the B channel, respectively.



**Figure 3.** Optimization of complexation parameters: (a) Sample pH; (b) Concentration of ligand; (c) Volume of sample solution; and (d) Complexation time. Optimum smartphone digital image colorimetry conditions: Type of phone, SM-C9; area of region of interest, 6400 px<sup>2</sup>; position of camera, side; and distance between sample and camera, 10.0 cm;  $R_B = 255 - I_B$ , where,  $R_B$  and  $I_B$  are the response and intensity of the analyte solution in the B channel, respectively.