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Exploring natural indicators: aronia berries and turmeric as eco-friendly and cost-effective alternatives for acid–base titrations

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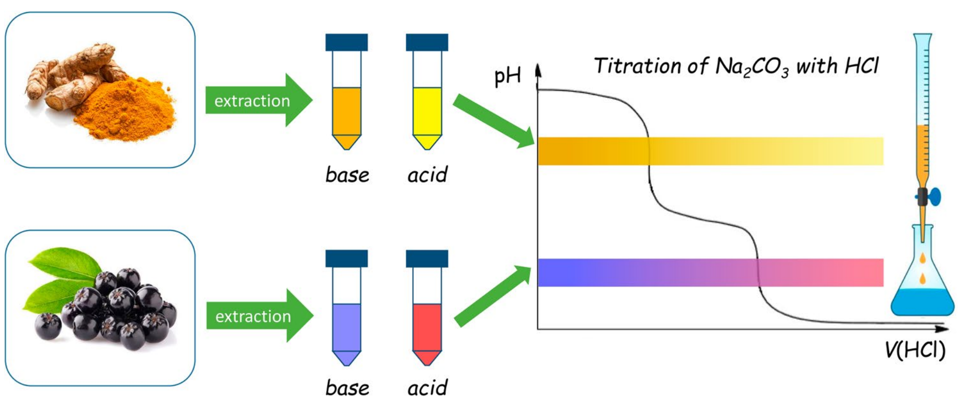
Abstract

This study investigates the potential of aronia (rich in cyanidins) and turmeric (containing curcumin) extracts as natural indicators for acid–base titrations. The extracts were characterized using HPLC/DAD/ESI-MS^n. For the first time, this study explores the use of natural indicators in the titrations of polyprotic acids and bases. Aronia extract exhibited a color change from pink (acidic) to turquoise (basic), with absorption maxima at 515 and 610 nm, respectively. It was effective for titrations involving weak bases with strong acids and polyprotic acids and bases, with relative errors around 0.5%. It was especially effective for determining the second end point in Na_2CO_3 titrations and the first end point in H_3PO_4 titrations, with relative errors around 1%. Turmeric extract demonstrated a yellow-to-orange color transition, with absorption maxima at 425 (acidic) and 460 nm (basic). It was effective for titrations of weak acids with strong bases and the first end point in Na_2CO_3 titrations, with errors under 1%. Turmeric was also suitable for the second end point in H_3PO_4 titrations, with a relative error around 2%. Both natural indicators showed promising results compared to synthetic indicators. Aronia extract can be used in acid–base titrations instead of methyl red, while turmeric extract can replace phenolphthalein.

Graphical Abstract



Keywords Natural indicators · Titrations · Analytical chemistry · Turmeric · Aronia

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Introduction

Natural indicators, derived from plant-based sources such as fruits, vegetables, and flowers, provide sustainable and eco-friendly alternatives to synthetic chemical indicators in analytical chemistry. These food-based colorants, rich in anthocyanins, flavonoids, carotenoids, and betalains, exhibit pH-sensitive color changes, making them valuable for various applications.

Natural indicators effectively replace synthetic pH indicators in acid–base titrations, reducing chemical waste and toxicity (Nag et al. 2023). In the food and beverage industry, they are used for quality control and freshness assessment, such as detecting spoilage in dairy products (Amjad et al. 2023a; Rodrigues et al. 2021). Additionally, they play a role in water quality testing by determining pH variations and pollution levels, contributing to environmental monitoring efforts (Amjad et al. 2023b). Ongoing research explores their integration into biosensor technology for detecting chemical changes in biological and industrial samples (Hassan et al. 2023). For educational and laboratory purposes, natural indicators offer a safe and accessible alternative for chemistry education, minimizing exposure to hazardous chemicals (Naimi et al. 2024).

This paper examines the application of natural indicators derived from food sources (aronia and turmeric) and their role in promoting green chemistry principles, including reduced toxicity, biodegradability, and sustainability in analytical chemistry laboratories. Specifically, it investigates the potential of aronia and turmeric as natural indicators for acid–base titrations. Both are widely cultivated, offering a more sustainable and accessible alternative to synthetic indicators, which often require complex production processes.

Titrations are fundamental to analytical chemistry courses, teaching students about the principles of stoichiometry, chemical reactions flow, and the selection and proper use of indicators. They reinforce students' understanding of concept of chemical reactions and equilibrium (Baldwin and Orgill 2019; Pinthong et al. 2022; Wang et al. 2024). A key aspect of titrations is the ability to accurately determine the endpoint, which should closely correspond to the equivalence point. Achieving this requires a good understanding of the shape of titration curves and the selection of an appropriate indicator.

Synthetic indicators such as methyl orange, methyl red, phenolphthalein, and bromothymol blue are commonly used in acid–base titrations (Bhuchar et al. 1971; Cardona and Magri 2014). While these indicators are effective, they raise environmental concerns due to their production, disposal, and potential toxicity, as well as issues related to cost and limited availability in certain contexts (Farhan Hanafi and Sapawe 2020; Vahabzadeh and Karimi 2024).

As an alternative, natural sources such as plants, animals, algae, and fungi provide pigments and chemicals that can be used as dyes or indicators (Nag et al. 2023). Numerous natural sources have been utilized to prepare indicators, such as butterfly pea, sweet potatoes, *Bougainvillea*, *Moringa*, hibiscus, turmeric, beetroot, and various flowers like *Clitoria ternatea*, *Catharanthus roseus*, and *Rosa* species (Asemave and Shiebee 2022; Caraballo et al. 2021; Ernawati 2022; Kadam et al. 2013; Musa et al. 2022; Okoduwa et al. 2015; Onuegbu et al. 2023; Thomas 2018).

Aronia's potential as a natural indicator stems from its high anthocyanin content, pigments that change color with pH (Zulfajri 2018). The color is primarily due to cyanidin derivatives, such as glucoside, galactoside, xyloside, and arabinoside (Petreska Stanoeva et al. 2020). Its natural abundance and color-changing properties make it a promising candidate for educational and environmental applications. Although aronia has been studied as a natural pH indicator (Aydogdu Emir et al. 2023; Roy and Rhim 2020; C. Wang et al. 2023), to our knowledge, there are no reported studies on its application in titrations.

Turmeric, a vibrant yellow spice from the rhizomes of *Curcuma longa*, belongs to the ginger family (*Zingiberaceae*). It typically contains 2–9% curcuminoids, including curcumin, demethoxycurcumin, bisdemethoxycurcumin, and cyclic curcumin. Curcumin, the primary component, is responsible for turmeric's indicator properties (Asemave & Shiebee 2022; Caraballo et al. 2021). It changes color from yellow in acidic conditions to reddish-brown in basic conditions, making it ideal for acid–base titrations (Asemave & Shiebee 2022). Beyond its culinary use, turmeric has a documented history of being used as a natural indicator as a natural indicator in scientific applications (de Sousa Silva et al. 2002; Asemave and Shiebee 2022; Onuegbu et al. 2023).

The main objectives of the study were to develop cost-effective, environmentally friendly natural indicators using ethanolic extracts of aronia and turmeric and to compare their effectiveness with synthetic indicators in acid–base titrations. The indicators were tested for their efficiency on strong and weak monoprotic acids and bases, as well as on polyprotic acids and bases. These natural alternatives could serve as valuable educational tools and sustainable options for pH monitoring in research and industry.

Experimental

Materials

Turmeric (*Curcuma longa* L.) powder and aronia (*Aronia melanocarpa)* were purchased from a local supermarket. Hydrochloric acid (HCl), acetic acid (CH_3COOH), phosphoric acid (H_3PO_4), sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH), and sodium carbonate (Na_2CO_3) solutions were used with a concentration of 0.1 mol/L. Ethanol and ascorbic acid were purchased from Alkaloid AD, North Macedonia. Phenolphthalein, methyl red, and methyl orange were used as 1% solutions in ethanol (Alkaloid AD, Skopje, North Macedonia).

For the pH measurements, a Mettler Toledo pH meter was used, and Agilent Carry 60 UV–Vis Spectrophotometer was used for obtaining UV–Vis spectra of the extracts.

Preparation of natural indicators

The indicator turmeric extract (TE) was prepared by weighing 2.5 g of turmeric powder into a glass beaker and adding 250 mL ethanol/water/ascorbic acid (70:28:2) solvent mixture. Ascorbic acid was included to lower the pH of the extracts and to ensure effective extraction of target compounds, as supported by previous research (Nag et al. 2023; Stanoeva et al. 2021). The extract was filtered and stored in a dark bottle. The aronia extract (AE) indicator was prepared similarly using homogenized fresh aronia fruits.

HPLC/DAD/ESI-MS^n analysis of natural indicators

The separation and identification of bioactive compounds in both extracts were carried out using HPLC/DAD/ESI-MS^n with an Agilent HPLC system, which was equipped with a UV–Vis diode-array detector and an ESI Ion Trap mass spectrometer. An Agilent Eclipse C18 column (150 × 4.6 mm, 5 µm) was utilized for the analysis.

For the turmeric extract, an isocratic elution was performed using a mobile phase composed of 2% (v/v) acetic acid in water (solvent A) and acetonitrile (solvent B) at a ratio of 35% B. The separation was conducted over 30 min at a flow rate of 2 mL/min. In the case of aronia extract, a gradient elution method was employed using the same mobile phase, with the following gradient program: 0–5 min, 5% B; 5–20 min, 5–35% B; 20–45 min, 35–50% B; 45–55 min, 50–70% B; and 55–60 min, 70–100% B. The flow rate was set at 0.4 mL/min, with an injection volume of 10 µL.

The structures of curcumin, demethoxycurcumin, and bisdemethoxycurcumin were confirmed based on their ESI–MS spectra in negative ionization mode, while the structures of cyanidin 3-glucoside, 3-arabinoside, and 3-xyloside were identified using their ESI–MS spectra in positive ionization mode.

Acid–base titrations

Both indicators were tested for their efficiency using six different solutions, including acids (HCl, CH_3COOH, H_3PO_4), bases (NaOH, NH_4OH), and a salt (Na_2CO_3), each with a concentration of approximately 0.1 mol/L. Classical acid–base titrations were performed using 10.00 (± 0.01) mL of each solution in an Erlenmeyer flask, with five drops of the respective indicator added. Different acid–base combinations were tested, as shown in Table 1. The mean titrant volume at the endpoint was calculated for each titration, which was performed in triplicate. The standard deviation was calculated, and the pH at each endpoint was measured. The accuracy of the natural indicators was compared to that of the most appropriate synthetic indicator, including methyl red (MR), methyl orange (MO), and phenolphthalein (PH).

The molar concentrations of each solution were calculated using the molar ratio of each chemical reaction occurring depending of titration curve.

Results and discussion

Characterization of natural indicators

The qualitative analysis confirms the presence of cyanidin derivatives, including cyanidin-3-glucoside, cyanidin-3-arabinoside, and cyanidin-3-xyloside, in aronia extract, as well as bisdemethoxycurcumin, demethoxycurcumin, and curcumin in turmeric extract. Data on retention time, UV maxima, and MS analysis are provided in Table 2, while the representative chromatograms of both extracts and MS spectra of all compounds are shown in Figs. S1 and S2, respectively.

The application of these indicators in different pH media demonstrates significant dependence on pH, resulting in noticeable color changes. The UV–Vis spectra revealed distinct absorption peaks under both acidic and basic conditions.

Table 1 Type of titration, reaction, and pH in equivalent point

Type	Titrand/Titrant	Reaction	pH in Equivalence point (calculated)
SB/SA	NaOH/HCl	$NaOH + HCl \rightleftharpoons NaCl + H_2O$	7.00
WB/SA	NH_4OH/HCl	$NH_4OH + HCl \rightleftharpoons NH_4Cl + H_2O$	5.27
BS/SA	Na_2CO_3/HCl	$Na_2CO_3 + HCl \rightleftharpoons NaHCO_3 + NaCl$	8.33
		$Na_2CO_3 + 2HCl \rightleftharpoons Na_2CO_3 + CO_2 + H_2O$	3.97
WA/SB	CH_3COOH/NaOH	$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$	10.98
WA/SB	H_3PO_4/NaOH	$H_3PO_4 + NaOH \rightleftharpoons NaH_2PO_4 + H_2O$	4.67
		$H_3PO_4 + 2NaOH \rightleftharpoons Na_2HPO_4 + H_2O$	9.77

WA—weak acid, WB—weak base, SA—strong acid, SB—strong base, BS—basic salt, AS—acidic salt

Table 2 Retention times, and characteristic ions of bioactive compounds in the natural indicators

Compound	t_R/min		MS^2
Aronia extract		$[M]^+$	
Cyanidin-3-glucoside	18.8	449	287
Cyanidin-3-arabinoside	19.6	419	287
Cyanidin-3-xyloside	20.4	419	287
Turmeric extract		$[M–H]^-$	
Bisdemethoxycurcumin	18.5	307	**187***, 143, 119
Demethoxycurcumin	21.5	337	**217**, 187, 173, 143, 119
Curcumin	25.1	367	265, **217**, 173, 157, 149

*The number in bold presents most abundant fragment ion

The aronia extract exhibited a pink color under acidic conditions and a turquoise color under basic conditions, with maximum absorption occurring at 515 nm in acidic media and 610 nm in basic media (Fig. 1a, 1b).

This spectral shift, characteristic of anthocyanin-rich extracts (Vankar and Bajpai 2010), is attributed to the protonation of the flavylium cation at low pH and its deprotonation at higher pH (Nag et al. 2023) (Fig. 2a). There are at least 23 naturally occurring anthocyanidins, with cyanidin, pelargonidin, peonidin, delphinidin, petunidin, and malvidin being the most prevalent. These compounds contain multiple hydroxyl groups that can undergo deprotonation in aqueous solutions, depending on the pH. Their acidity is defined by their acid-dissociation constants (K_a), which play a crucial role in determining their chemical properties and reactivity. For compounds with multiple acidic sites, different deprotonation behaviors may occur, making the system more complex (Hassan et al. 2023). Additionally,

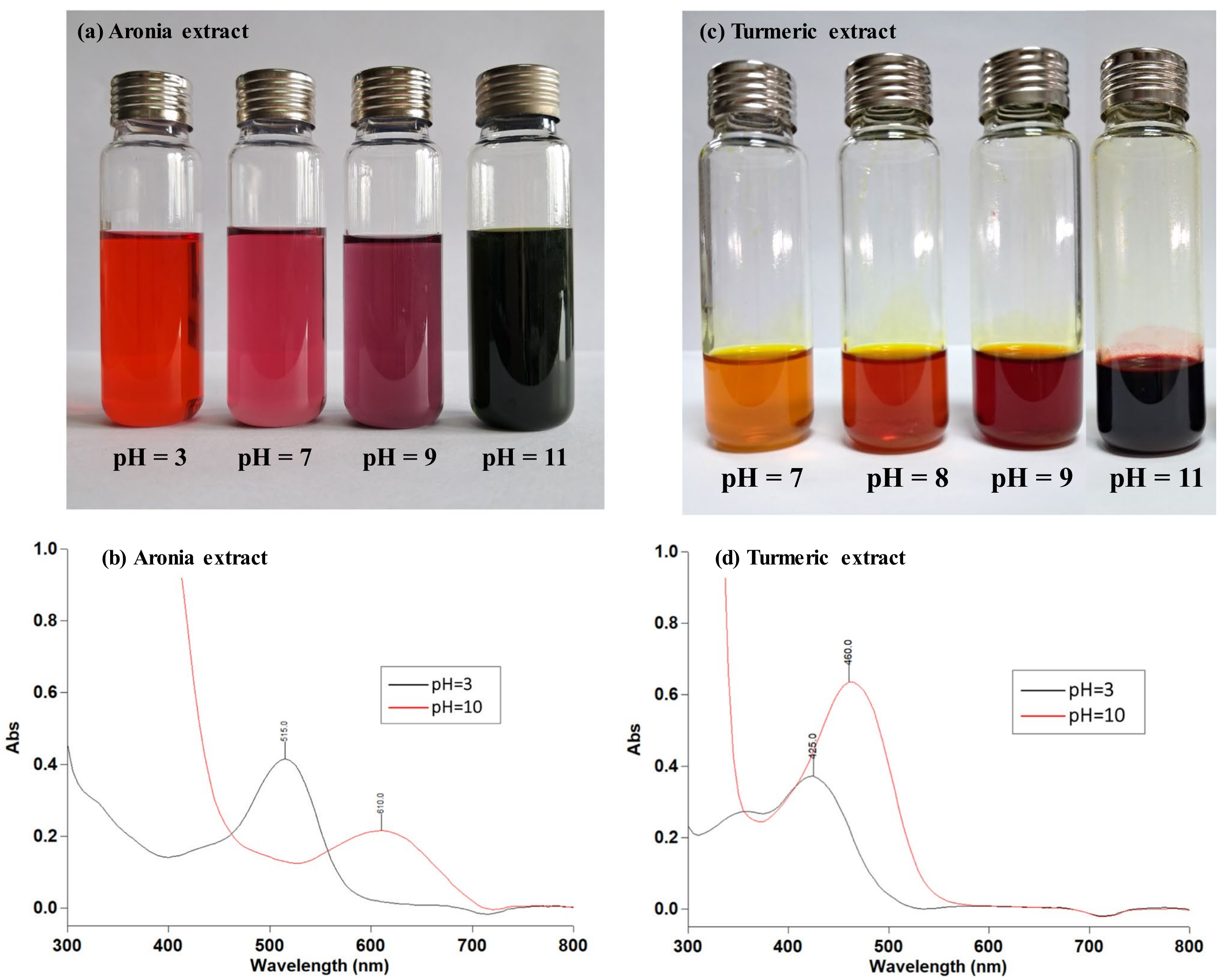

Fig. 1 Colors change and UV–Vis spectra of **a**, **c** aronia extract and **b**, **d** turmeric extract in acid and base media

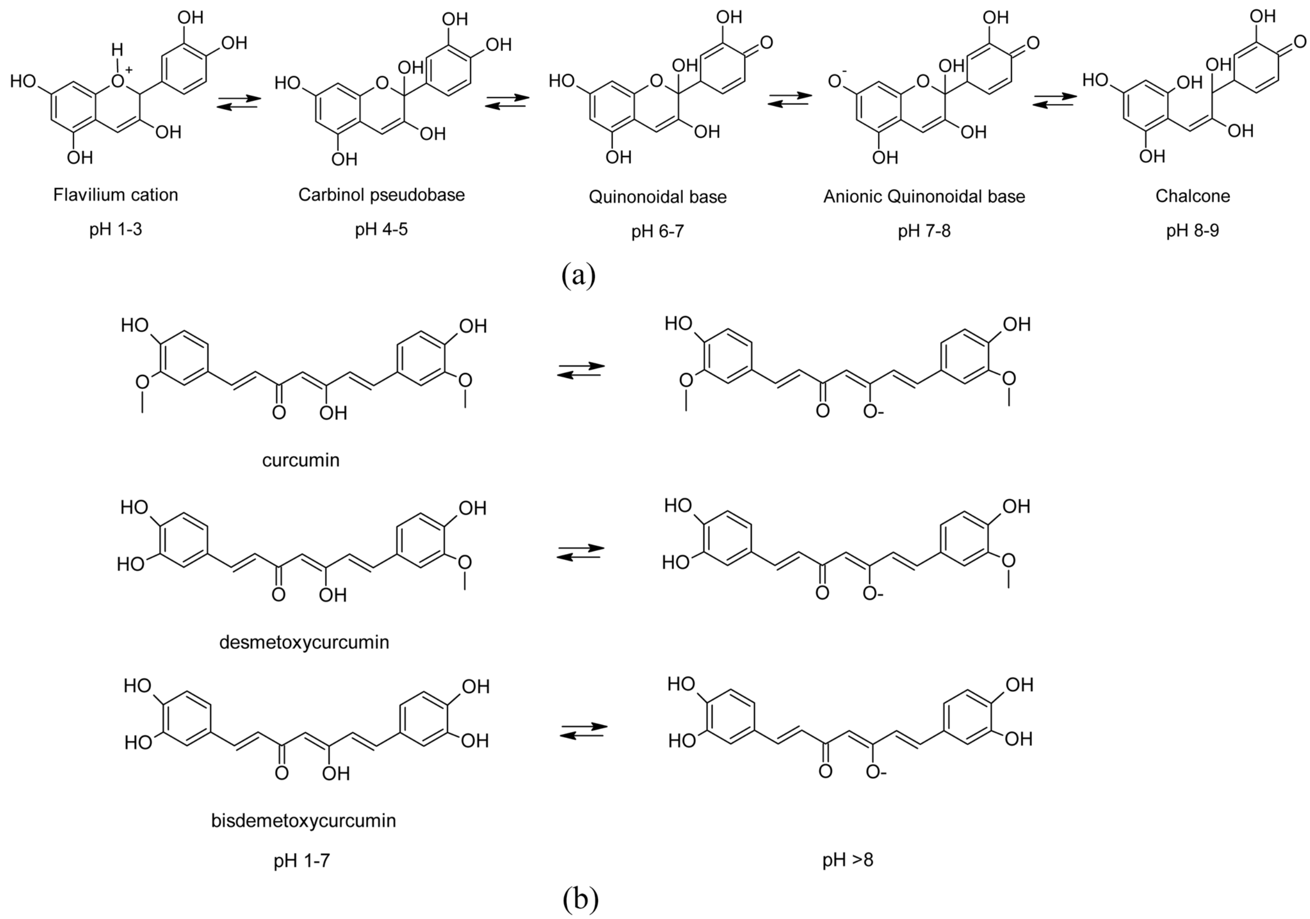

Fig. 2 Structural changes depending on pH in the main compounds of **a** aronia extract (cyanidin) and in **b** turmeric extract (bisdemethoxycurcumin, demethoxycurcumin, and curcumin)

anthocyanidins can be conjugated with various phenolic acids, further increasing their structural complexity and the number of pK_a values. This complexity can pose challenges for their application in acid–base titrations and quantitative analysis.

For this reason, while different fruits can serve as natural pH indicators, aronia is particularly suitable fruit for preparing natural indicator for acid–base titrations because it contains only cyanidin as its anthocyanidin, simplifying its acid–base behavior. For cyanidin, the appropriate pK_a value for use in acid–base titrations is 5.48 (León-Carmona et al. 2016).

Turmeric extract showed a bright yellow color in acidic media and orange in basic media, with maximum absorption at 425 nm (acidic) and 460 nm (basic) (Fig. 1c). The spectral changes are attributed to the keto-enol tautomerism and prototropic equilibria of curcumin, demetoxycurcumin, and bisdemetoxycurcumin (de Sousa Silva et al. 2002) (Fig. 2b). Curcumin, the most abundant component in the extract, has a pK_a value of 8.56, which is higher than that of cyanidin. This property is one of the reasons why this natural indicator was included in the study.

Acid–base titrations using natural indicators

By understanding the pH change behavior of titration curves and considering an indicator's pK_a and its pH range of color change, a suitable indicator can be selected for the specific titration. The rate of pH changes in the titration curve depends on the strength of the acid and base being titrated, which directly affects the appropriateness of the indicator. For a distinct color change, the indicator's pK_a should closely match the expected pH at the equivalence point. The pK_a values of the synthetic indicators methyl orange, methyl red, and phenolphthalein are 3.46, 5.0, and 9.3, respectively, whereas the pK_a values for the most abundant components of the natural indicators, cyanidin and curcumin, are 5.48 and 8.56, respectively. Based on these pK_a values, the aronia extract should serve as a natural alternative to methyl red, while the turmeric extract should be a natural alternative for phenolphthalein.

Due to the distinct color changes in different pH media, turmeric and aronia extracts were tested for detecting the endpoints of simple acid–base titrations. The results were compared with those obtained using standard indicators: methyl red, methyl orange, and phenolphthalein. The complete titrations results are given in Table 3.

The simplest type of titration is between a strong acid and a strong base. The pH at the equivalence point is around 7, and the change in the titration curve is sharp and well-pronounced. For this reason, the determination of the end point is not strongly related to the pK_a of the indicator, making many indicators suitable for this type of titration. In the NaOH-HCl titration, both tested natural indicators accurately detected the end point. The experimental errors for turmeric extract (TE) and aronia extract (AE), compared to methyl red as the standard indicator, were 0.34 and − 1.53%, respectively. A color change from orange to yellow was observed with turmeric, and from turquoise to pink with aronia. Comparative results demonstrate the suitability of turmeric as an indicator for strong acid–strong base titrations (Asemave and Shiebee 2022). Previous research on the use of anthocyanins as end-point indicators reported relative errors between 0.1 and 1.0% (Vankar and Bajpai 2010).

During the titration of a weak base with a strong acid, the reaction product is an acidic salt, and the pH at the equivalence point is below 7. In our case, during the titration of NH_4OH (a weak base, ($K_b = 1.8 \times 10^{-5}$ mol/L)) with HCl (a strong acid), the theoretical pH value at the equivalence point should be 5.27. For this reason, methyl red ($pK_a = 5.0$) is the most suitable synthetic indicator for this type of titration. Comparing the results of natural indicators to those of methyl red, it is evident that aronia extract performed better, showing an experimental error of -0.54%, whereas turmeric extract cannot be used as an indicator for this type of titration.

In contrast, during the titration of a weak acid with a strong base, the pH at the equivalence point is above 7. In our case, for the titration of CH_3COOH ($K_a = 1.8 \times 10^{-5}$ mol/L) with NaOH, the theoretical pH at the equivalence point is 10.98. Turmeric extract is suitable for this type of titration, with an experimental error of 0.92%, and can be used as an alternative to phenolphthalein.

Sodium carbonate, Na_2CO_3 ($K_{b1} = 2.13 \bullet 10^{-4}$, $K_{b2} = 2.27 \bullet 10^{-8}$ mol/L), dissociates in water in two steps. In the titration curve, two equivalence points can be identified: the first equivalence point at pH 8.33, resulting from

Table 3 Titration results of turmeric and aronia extracts, as well as commercial indicators

Type	Titrand/Titrant	Indicator	pH in Equivalence point	*V* (titrant)/mL	*c*/mol/L	*E*/%	pH in End point	Color change
SB/SA	NaOH/HCl	**MR**	**7.00**	**9.78 ± 0.03**	**0.10390[a]**		**6.45**	**Yellow–light pink**
		TE		9.73 ± 0.12	0.10425[a]	0.34	6.55	Orange–yellow
		AE		9.63 ± 0.15	0.10231[a]	− 1.53	7.25	Turquoise–pink
WB/SA	NH_4OH/HCl	**MR**	**5.27**	**18.60 ± 0.00**	**0.19753[b]**		**6.22**	**Yellow–Light pink**
		MO		17.17 ± 0.06	0.18231[b]	− 7.71	3.86	Yellow–Orange
		TE		18.50 ± 0.00	0.17842[b]	− 9.60	6.06	Orange–yellow
		AE		16.80 ± 0.00	0.19647[b]	− 0.54	6.42	Turquoise–pink
BS/SA	Na_2CO_3/HCl	**PH**	**EP1 8.33**	**10.90 ± 0.12**	**0.10533[c]**		**9.45**	**Colorless–light pink**
		TE		11.00 ± 0.20	0.10437[c]	0.90	8.00	Orange–yellow
		MO	**EP2 3.97**	**18.50 ± 0.10**	**0.10620[c]**		**3.55**	**Yellow–Orange**
		MR		18.49 ± 0.12	0.10618[c]	0.05	6.53	Yellow–light pink
		AE		21.80 ± 0.26	0.09012[c]	0.92	6.19	Turquoise–pink
WA/SB	CH_3COOH/NaOH	**PH**	**10.98**	**9.37 ± 0.12**	**0.09732[d]**		**9.59**	**Colorless–light pink**
		TE		10.50 ± 0.00	0.10494[d]	0.92	9.42	Yellow–orange
		AE		10.10 ± 0.06	0.10910[d]	12.10	7.19	Pink–turquoise
WA/SB	H_3PO_4/NaOH	**MR**	**EP1 4.67**	**9.99 ± 0.05**	**0.10346[e]**		**3.88**	**Red–orange**
		MO		9.73 ± 0.06	0.10076[e]	− 2.60	4.28	Red–orange
		AE		10.12 ± 0.87	0.10480[e]	1.30	6.67	Pink–turquoise
		PH	**EP2 9.77**	**21.03 ± 0.21**	**0.10889[e]**		**9.1**	**Colorless–light pink**
		TE		20.53 ± 0.21	0.10630[e]	− 2.38	8.81	Yellow–orange

Standard indicators are underlined in bold.

WA—Weak acid, WB—Weak base, SA—Strong acid, SB—Strong base, BS—Basic salt, AS—Acidic salt, MR—Methyl red, MO—Methyl orange, PH—Phenolphthalein, TE—Turmeric extract, AE—Aronia extract

[a] *c*(NaOH), [b] *c*(NH_4OH), [c] *c*(HCl), [d] *c*(CH_3COOH), [e] *c*(H_3PO_4)

the formation of $NaHCO_3$, and the second equivalence point at pH 3.97 due to the formation of CO_2. Phenolphthalein ($pK_a = 9.3$) is the most suitable synthetic indicator for determining the first equivalence point, and methyl orange ($pK_a = 3.46$) is considered best for determining the second equivalence point. For the natural indicators applied, both were suitable for the titration: turmeric extract ($pK_a = 8.56$) for the first end point and aronia extract ($pK_a = 5.48$) for the second end point, with relative errors compared to the corresponding synthetic indicators of 0.90 and 0.92%, respectively.

The titration of H_3PO_4 with NaOH presents an interesting case. Although phosphoric acid is triprotic ($K_{a1} = 7.1•10^{-3}$, $K_{a2} = 6.3•10^{-8}$, $K_{a3} = 4.5•10^{-13}$ mol/L), it can be titrated as either monoprotic or diprotic acid. The titration curve features two infliction points, which are typically detected using methyl orange (for the first) and phenolphthalein (for the second) (Farhan Hanafi and Sapawe 2020). Turmeric extract (TE) was expected to perform well in detecting the second endpoint (calculated pH = 9.77) due to pK_a values of 8.55 and 10.4 (Nag et al. 2023). The results showed a relative error of -2.38% when turmeric extract (TE) was used for the determination of the second end point, compared to phenolphthalein. On the other hand, the relative error for the determination of the first end point with aronia extract (AE) provided better accuracy, with an error of 1.3% compared to methyl red. This study presents the first report on the application of natural indicators for acid–base titrations of polyprotic acids and bases.

Conclusions

This study explored the potential of turmeric and aronia extracts as eco-friendly and cost-effective natural indicators for acid–base titrations, comparing their performance with standard synthetic indicators. Both natural indicators demonstrated distinct color changes depending on the pH of the medium, with turmeric showing a bright yellow-to-orange transition and aronia exhibiting a pink to turquoise change.

Experimental results confirmed their effectiveness in acid–base titrations. Both extracts can be used for titrating strong acids and bases. Turmeric extract is suitable for titrating weak acids with strong bases and for determining the first end point in Na_2CO_3 as a polyprotic base, with relative errors of less than 1%. It can also be used for determining the second end point in the titration of H_3PO_4, though with a relative error around 2%.

Aronia extract is suitable for titrating weak bases with strong acids (with a relative error of about 0.5%) and can also be used for titrations involving polyprotic acids and bases. The relative errors in determining the second end point in the titration of Na_2CO_3, and the first end point in the titration of H_3PO_4, are around 1%.

Overall, these findings support the use of turmeric and aronia extracts as sustainable alternatives to synthetic indicators. Their application promotes environmental awareness, aligns with green chemistry principles, and offers valuable teaching aids in educational settings. Future research could further explore their potential, advancing their use in more complex titration systems.

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Declarations

Conflict of interest The authors of this manuscript declare no conflict of interest.

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