Analysis of Phenolic Compounds by Coulometric Array Detector

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Contributor: Mutasem Razem, Yubin Ding, Ksenia Morozova, Fabrizio Mazzetto, Matteo Scampicchio

Phenolic compounds are an important group of organic molecules with high radical scavenging, antimicrobial, anti-inflammatory, and antioxidant properties. The emerging interest in phenolic compounds in food products has led to the development of various analytical techniques for their detection and characterization. Among them, the coulometric array detector is a sensitive, selective, and precise method for the analysis of polyphenols.

Keywords: phenolic compounds ; coulometric array detector ; electrochemical sensors

1. Fruits

The antioxidant activities of currant and gooseberry grown under an organic regime and in integrated pest management orchards were determined and compared by using the flow injection analysis method with a CoulArray detector [1]. The CoulArray consisted of four working porous graphite electrodes and reference hydrogen–palladium electrodes. The potentials of the electrodes were at +200, +400, +600, and +800 mV vs. the Pd pseudo-reference electrode, with the antioxidant capacity expressed as the electrical charge in C (Coulombs) per gram of fresh weight of fruit. The Triton black currant, grown in an organic orchard, had the highest antioxidant activity, with a value of 0.785 C g^{-1}; the Jesan red currants had a value of 0.226 C g^{-1}; and the Blanka white currant had a value of 0.356 C g^{-1}.

Hajazimi et al. also determined different phenolic acids and flavonols in berries using the HPLC–CoulArray method [2]. Lingonberry, cloudberry, bilberry, and seabuckthorn berry are common berries consumed in the Nordic diet that contain a rich amount of dietary fiber; vitamins C, E, and K; polyphenols; and other bioactive compounds [3]. The flavonols quercetin, myricetin, kaempferol, and isorhamnetin and the gallic, vanillic, ferulic, *p*-coumaric, and caffeic phenolic acid aglycones of the berry species were determined. An ESA 5600A coulometric detector with eight porous graphite electrodes was used. The potentials that were applied were 0, +120, +240, +360, +480, +600, +720, and +840 mV. Sea-buckthorn berry contained the highest amount of the selected phenolic compounds with 270.5 mg/100 g DW, along with lingonberry with 219.7 mg/100 g DW. Cloudberry had the highest amount of hydroxybenzoic acid (66.8 mg/100 g), while bilberry demonstrated the richest amount of hydroxycinnamic acid (136.5 mg/100 g) and was especially abundant in caffeic and p-coumaric acids.

In a study carried out by Pyo et al., a reversed-phased HPLC coupled with a coulometric array detector was used to determine and characterize 13 different phenolic compounds from methanol extracts of Swiss chard (*Beta vulgaris* subspecies *cycla*) [4]. Standard solutions of nine phenolic acids and four flavonoids were prepared to compare with the Swiss chard samples and investigate their reproducibility and sensitivity. The sensitivity of the detection limit in this research was 1 ng mL^{-1}. Moreover, the phenolic acids gave signals at low potentials (+70–+375 mV), excluding p-hydroxybenzoic acids, which responded at a potential of +825 mV vs. palladium reference electrodes. The total concentration of phenolics found in red Swiss chard was 157.8 mg/100 g FW, and in white Swiss chard it was 124.7 mg/100 g FW. Syringic acid was the most abundant phenolic compound found in both red and white leaf extracts. **Table 1** indicates the different phenolic compounds found in different food items using a CoulArray detector.

The polyphenol profile of edible honeysuckle berries (*Lonicera edulis*) was also evaluated using a 12 channel CoulArray detector [5]. The honeysuckle is an uncommon fruit species mainly found in Russia that contains high contents of vitamin C and polyphenols [6]. The polyphenolic compounds that were discovered using the CoulArray detector were gallic acid, catalposide, rutin, resveratrol, quercitrin, chlorogenic acid, and quercetin, chlorogenic acid being the major antioxidant present (182 mg/kg FW), as expected by Jurikova et al. [7].

Strawberries (*Fragaria* × *ananassa*) are also known to have high quantities of phenolic compounds, mainly anthocyanins, as these are responsible for the red color of the fruit [8]. An eight-channel CoulArray detector with potentials set from +100

to +800 mV in increments of +100 mV was used to characterize the polyphenolic profile of strawberries [9]. The responses of the compound concentrations were plotted versus the oxidation potential in hydrodynamic voltammograms (HDVs) to characterize the polyphenols present. The selected phenolic compounds found in strawberry fruits included catechin, *p*-coumaroylhexose, and hydroxybenzoylhexose.

2. Herbs

Since ancient times, herbs have been used for culinary and medicinal purposes as they can prevent chronic diseases [10]. This is mainly due to the presence of phytochemicals with high antioxidant activity. Alkaloids, polyphenols, and carotenoids have been found in numerous officinal plants [11]. The antioxidants present in these plants can be evaluated using specific assays, such as 2,2-diphenyl-1-picrylhydrazyl (DPPH), ferric-reducing antioxidant power (FRAP), and oxygen radical absorbance capacity (ORAC) assays [12]. For better characterization and selectivity of the antioxidant species present, the coupling of HPLC with coulometric array detectors (CADs) has been applied.

Ding et al. screened several antioxidant compounds in 19 officinal plants using HPLC-DAD-CAD-MS, with the CoulArray detector consisting of 16 porous graphite cells increasing from −50 to +700 mV with +50 mV increments [13]. The use of 16 electrodes in series resulted in an increase in the dynamic range of the CoulArray detector. *Moringa oleifera* was used to compare the antioxidant compounds with the other officinal plants due to it being a rich source of phenolic compounds. The most dominant antioxidant species present in the *Moring oleifera* extract was hyperoside, followed by neochlorogenic acid. With the use of Faraday's law, the concentration of each antioxidant compound was determined. The total charge (Q_{tot}) of each plant extract was obtained by summing up all the 16 channels of the CoulArray detector, as the total (Q_{tot}) indicates the total antioxidant capacity of each plant extract. The *Melissa officinalis* and *Fraxinus excelsior* herbs had the highest Q_{tot} at 1900 and 2646 µC, respectively. The CoulArray detector was also used to determine phenolic compounds in several aromatic plants [14].

Different phenolic compounds were also identified using an eight-channel CoulArray detector in tea samples [15]. The applied potentials for the eight cells of the CoulArray detector ranged from +250 to +900 mV. 4-Hydroxycoumarin was the most abundant antioxidant compound in all 11 tea samples analyzed in the latter study. However, syringic and ferulic acids had the lowest concentrations among the phenolic compounds in the tea samples.

3. Beverages

Many bioactive compounds can be found in beverages due to the diverse components present in drinks. The phenolic compounds present in beverages originate from the plant or fruit used during their production, such as barley or hops for beer and honey for mead. A 16 channel CoulArray detector was used for the analysis of several phenolic compounds in juices and other beverages [16][17]. An HPLC-CAD with 8 porous graphite working electrodes was used for the analysis of phenolic compounds in wines and meads [18]. The potentials of the electrochemical cells were set in the range from +200 to +900 mV at +100 mV increments. The limit of detection for the phenolic compounds that were analyzed was 2.8–15.0 µg L^{-1}. The compounds that were detected were derivatives of cinnamic and benzoic acid. Vanillin had the highest concentration among all the phenolic compounds from the mead samples (0.570–5.171 mg L^{-1}). In white wines, the highest concentration among the phenolic compounds detected was for rutin (0.875–5.078 mg L^{-1}).

In another study performed by Kahoun et al., a CoulArray detector with eight channels was used to detect different phenolic compounds in mead samples, benzoic acid hydroxyderivatives being the most common phenolic compounds [19]. Vanillin and ethyl vanillin contributed significantly to the sensory attributes of the different mead samples. Vanillin is normally detected in trace amounts, as it originates from honey or propolis. Higher concentrations can indicate the addition of vanillin intentionally, as found in samples of almond meads in the previous study. The phenolic content in mead is based on its composition and storage conditions. Another study analyzed phenolic compounds and flavonoids in beer samples using 11 different columns with different stationary phases in an HPLC system coupled to an eight-channel CoulArray detector [15] The potentials of the electrodes were set from +250 to +900 mV.

A comparative study was undertaken by Bocchi et al. for the determination of several polyphenolic compounds in a brandy sample using UV and coulometric detectors coupled with HPLC [20]. The working electrodes were set from −150 to +900 mV. The sensitivity and selectivity of the phenolic compounds were greater using the CoulArray detector than the UV, as the CoulArray detector was able to monitor the responses of all the phenolic acids due to the low limit of detection (1–5 µg L^{-1}). The content of the phenolic acids presented ranged from 3.1 to 140 µg L^{-1}.

4. Cereals

Not much research has been undertaken regarding the determination of phenolic compounds in cereals using a coulometric detector. Polyphenols in cereals do not just act as antioxidant compounds but also play a role in the prevention of parasitic and pathogenic bacteria, which results in extended shelf-life and preservation. This may vary depending on the type of grain used, as phenolic compounds are mainly found in the bran or cortical layer of grains, such as in rice. Ferulic acid is a common phenolic compound that is mainly found in its bound form, as it is associated with the fibre content in the cereal [21]. However, the bioavailability of phenolic compounds is still being investigated, as some studies have shown that the phenolic compounds present in cereals may change when processed or cooked [22]. Most cereals are consumed after cooking in water or baking. For example, free phenolic compounds may be leached from pasta when boiled, as they are water-soluble. On the other hand, increased temperature through cooking may alter molecular structure and texture and can breakdown cellular components, resulting in an increase in bound phenolics in the food matrix [23]. More attention should be paid to the detection and characterization of phenolic compounds in raw and processed cereals using the CoulArray detector, as very few studies have been conducted.

Dvořáková et al. used HPLC coupled with an electrochemical eight-channel CoulArray detector to quantify free phenolic compounds in barley and malt extracts [24]. The potentials that were applied to the electrochemical cells were +250, +300, +400, +500, +600, +700, +800, and +900 mV. Seventeen phenolic compounds were identified and quantified from all the barley and malt varieties. They included (+)-catechin, (−)-epicatechin, esculin, umbeliferone, scopoletin, rutin, and quercetin, along with gallic, protocatechuic, p-hydroxyphenyl-acetic, vanillic, chlorogenic, caffeic, syringic, p-coumaric, ferulic, and sinapinic acid. Ferulic acid was the most abundant free phenolic compound that was present in barley and malt, with concentrations varying from 12.5 to 21.9 and 7.8 to 56.1 µg g^{-1} DW for barley and malt, respectively. Moreover, the concentration of catechin was related to the presence or absence of the hull in barley and malt. In hulled genotypes, the catechin content was 11.0–15.5 µg g^{-1} DW for barley and 0.9–5.9 µg g^{-1} DW for malt, which were lower in comparison to dehulled genotypes (15.0–17.0 µg g^{-1} DW for barley and 10.6–12.1 µg g^{-1} DW for malt).

An analysis of alkylresorcinols (AR) from different cereals using HPLC-CAD was undertaken by Ross and Kochhar [25]. Alkylresorcinols are phenolic lipids that can be found in the bran of barley, wheat, and rye kernels. The CoulArray detector had eight electrodes, which had their potentials set from 0 to +850 mV. The AR quantity differed between cereal samples, as the concentration in refined wheat flour samples ranged from 13–47 µg g^{-1}, which differed from that of wholegrain flours (489–660 µg g^{-1}).

5. Others

Spice plants—namely, parsley roots and leaves, celery roots and leaves, onion, and dill leaves—were analyzed to determine their antioxidant activities using HPLC coupled with a model 5600 CoulArray with an array of four detection cells [26]. The electrochemical detector had the working electrodes' potentials set at +300, +500, +700, and +900 mV. The flow rate of the mobile phase was set at 0.75 mL min^{-1} at the gradient of the phenolic compounds for 51 min. Chlorogenic acid was identified as the largest elution peak and the celery leaves contained the most phenolic compounds among the various spice vegetables.

The determination of the phenolic compounds in tomatoes was undertaken by Schindler et al. using a 16-channel electrode CoulArray detector [27]. The potentials applied were between +50 to +750 mV with an LOD of 6 µg L^{-1}, and the authors were able to detect several phenolic compounds (naringenin, rutin, ferulic acid, *p*-hydroxybenzaldehyde, and *p*-coumaric acid).

The analysis of flavonoids and polyphenols in almonds was undertaken using an HPLC-CAD with 13 working electrodes and potentials set from +60 to +720 mV with +60 mV increments [28]. A wide range of phenolic acids were identified and verified using LC-MS, including catechin, protocatechuic acid, epicatechin, and quercetin. The CoulArray detector has also been used to investigate the phenolic profile in oils [29][30]. Bayram et al. selected eight phenolics to be quantified from olive oil samples (caffeic acid, vanillic acid, ferulic acid, p-coumaric acid, oleuropein, tyrosol, hydroxytyrosol, and pinoresinol) using a 4 channel coulometric array detector with potentials set at +250, +400, +500, and +750 mV, respectively. In all the oil samples from the latter study, the concentration of the total phenolic compounds did not exceed 1.7 mg kg^{-1} oil, which was in accordance with a previously conducted study that found concentrations below this amount [31]. The use of an electrochemical detector for the analysis of phenolic compounds in oil is effective, reliable, and suitable for oil adulteration determination.

Based on the analytical information obtained from the literature and shown in **Table 1**, the detection limits vary based on the type of sample being analyzed. It is not surprising that complex samples contain different phenolic compounds and elute with different retention times. The majority of the authors who have used chromatographic methods have employed a linear gradient with a constant flow coupled with a CoulArray detector when analyzing phenolic compounds. The use of other detection methods, such as UV absorption, is still considered to be more common. Diode array detectors are also applied due to their ability to obtain complete UV–Vis spectra of the analytes and the possibility of selecting a specific wavelength. However, the main challenge when using these detectors is acquiring the best possible detection limits and quantitation, especially for complex chemical structures, such as phenolic compounds. The alternative approach is the application of CoulArray detectors or mass-spectrometry techniques. The use of mass spectrometry with HPLC allows the possibility of obtaining the phenolic fractions of different food matrixes with a broader linear range. Gas chromatography (GC) can also be applied for the determination and quantification of phenolic compounds and is more suitable if the phenolic compounds undergo derivatization to increase their volatility. However, the CoulArray detector is a very sensitive technique when it comes to the detection of phenolic compounds. Since phenolic compounds demonstrate electrochemical behavior, the CoulArray can use lower detection potentials and have lower detection limits than DAD and UV detection. On the other hand, mass spectrometry-related techniques are more selective, as more information about the molecular weight and structure can be obtained. The coupling of the CoulArray detector with mass spectrometry allows the CoulArray to work as a reactor. The combination of an electrochemical detector with mass spectrometry opens more doors to understanding redox potentials, the antioxidant activities of substances and individual phenolic compounds from complex food samples.

Table 1. Examples of phenolic compounds detected in food and beverages by the coulometric array detector.

Food Product Type	Food Matrix	Method	Working Electrode and Potential Range	Recovery %	Reproducibility (Coefficient of Variation (CV))	Limit of Detection (LOD)	Compounds	Reference
Fruit	Currant, gooseberry	FIA-ECD	4 PGEs, +200 to +800 mV	N/A	N/A	N/A	N/A	[1]
Fruit	Bilberry, lingonberry, cloudberry, seabuckthorn berry	RP-HPLC, gradient elution	8 PGEs, 0 to +840 mV	76.4% to 153.8%	N/A	N/A	Gallic acid vanillic acid caffeic acid p-coumaric acid Ferulic acid, myricetin, quercetin, isorhamnetin	[2]
Fruit	Swiss chard	RP-HPLC, gradient elution	2 PGEs, −50 to +825 mV	N/A	0.06%–1.05% CV	1 ng mL^{-1}	Gallic acid, vanillic acid, caffeic acid, p-coumaric acid, ferulic acid, myricetin, quercetin, p-OH-benzoic acid, proto-catechuic acid, chlorogenic acid, syringic acid, catechin, kaempferol	[4]
Fruit	Blue honeysuckle Saskatoon berry Chinese hawthorn	RP-HPLC, gradient elution	12 PGEs, −80 to +800 mV	N/A	N/A	N/A	N/A	[32]
Fruit	Honeysuckle berries	RP-HPLC, N/A	12 PGEs, N/A	N/A	N/A	N/A	Gallic acid, catalposide, rutin, resveratrol, quercitrin, chlorogenic acid	[5]

Food Product Type	Food Matrix	Method	Working Electrode and Potential Range	Recovery %	Reproducibility (Coefficient of Variation (CV))	Limit of Detection (LOD)	Compounds	Reference
Fruit	Strawberries	RP-HPLC, gradient elution	8 PGEs, +100 to +800 mV	N/A	N/A	N/A	Catechin, cinnamic acid derivatives, anthocyanin derivatives	[8]
Herbs	*Moringa oleifera, Melissa officinalis, Fraxinus excelsior,* and other officinal plants	RP-HPLC, gradient elution	16 PGEs, −50 to +700 mV	N/A	1.5% to 2%	1.3 ± 0.1 µM	Chlorogenic acid, isoquercetin, phloretic acid, oleuropein, osivitexin, gallic acid, catechin, protocatechuic acid, and others	[13]
Beverages	Red and white wines, meads	RP-HPLC, gradient elution	8 PGEs, +200 to +900 mV	N/A	N/A	2.8 to 15.0 µg L^{-1}	Cinnamic acid derivatives, benzoic acid derivatives, and others	[18]
Beverages	Meads	RP-HPLC, gradient elution	8 PGEs, +200 to +900 mV	N/A	N/A	4 to 29 µg L^{-1}	Gallic acid, protocatechuic acid, gentisic acid, vanillic acid, caffeic acid, syringic acid, *p*-coumaric acid, and others	[19]
Beverages	Beer, tea	RP-HPLC, gradient elution	8 PGEs, +250 to +900 mV	N/A	N/A	1 to 5 µg L^{-1}	4-Hydroxycoumarin, gallic acid, vanillic acid, rutin, caffeic acid, naringenin, and others	[15]
Cereals	Barley and malt extracts	RP-HPLC, gradient elution	8 PGEs, +250 to +900 mV	N/A	N/A	N/A	(+)-Catechin, (−)-epicatechin, esculin, umbeliferone, scopoletin, rutin, quercetin, and others	[24]
Cereals	Wholegrain wheat flour, wheat semolina. barley, rye bran, spelt, oats	RP-HPLC, gradient elution	8 PGEs, 0 to +850 mV	98.4% to 107.5%	0.8% to >10% CV, depending on the different homologues	1 ng g^{-1}	Alkylresorcinols	[25]
Spices	Parsley celery onion dill leaves	RP-HPLC, gradient elution	4 PGEs, +300 to +900 mV	N/A	N/A	4.75 µg mL^{-1}	Chlorogenic acid	[26]
Fruit	Tomatoes	RP-HPLC, gradient elution	16 PGEs, +50 to +750 mV	81.1% to 89.8 ±2.8%	N/A	3 to 13 µg mL^{-1}	Naringenin, rutin, ferulic acid, *p*-hydroxybenzaldehyde, *p*-coumaric acid, and others	[27]
Fruit	Almonds	RP-HPLC, gradient elution	13 PGEs, +60 to +720 mV	N/A	1.24% to 5.17%	N/A	Catechin, procatechuic acid, epicatechin, quercetin, and others	[28]
Oils	Olive oil	RP-HPLC, gradient elution	4 PGEs, +250 to +750 mV	N/A	N/A	0.03 to 1.7 ng mL^{-1}	Tyrosol, hydroxytyrosol, oleuropein, pinoresinol, caffeic acid, ferulic acid, vanillic acid, *p*-coumaric acid	[30]

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