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Determination of Cardanol- An Agricultural By-Product by Simple and Sensitive Spectrophotometric Method

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ABSTRACT:
Cardanol, a phenolic compound is found in cashew nut shell liquid (CNSL.) a by-product of cashew industry. It holds considerable promise because of its large availability in tropical areas, low cost, biodegradability and structural characteristics. Simple, sensitive, selective, rapid and reliable spectrophotometric method for the determination of cardanol, an agriculture by-product has been developed. The method describes the reaction of cardanol with iron (III) and subsequent reaction with ferricyanide to yield a Prussian Blue product with a maximum absorption at 730 nm. The method obeys Beer's law. As many as ten independent anions and cations did not interfere with the determination.

Introduction: Cardanol (3-pentadecenyl phenol) is a phenolic compound with C_{15} aliphatic chains in the meta position. It is a mixture of saturated and unsaturated (mono-, di- and tri-) compounds [commonly found in cashew nut shell liquid (CNSL), an alkyl phenolic oil which constitutes 25% of the total weight of cashew nut (Anacardium occidentale) a well-known species of the Anacardiaceae family. CNSL is obtained as a by-product of cashew industry, and is an important source of unsaturated hydrocarbon phenol.
Objectives: The work described in this paper forms part of a systematic investigation to develop new spectrophotometric methods for agri products - a field of paramount importance due to easy biodegradability and use of agricultural waste and by-products, in place of toxic chemicals - an area of current interest in environmental management.

Methods: Aliquots of standard solutions of cardanol and 2.0 ml each of iron (III) chloride and potassium ferricyanide were taken in 25-ml calibrated flask. The contents were mixed well and kept aside for 20 min at room temperature. It was then diluted to 25-ml mark with distilled water and the absorbance was measured at 730 nm against the corresponding reagent blank and calibration graph was constructed.

Results: The method is based on the reaction of cardanol with iron (III) salts in the presence of potassium ferricyanide in neutral medium to form a Prussian Blue (PB) product.

Conclusions: One of the recent frontiers of sustainable development has been the utilization of agricultural by-products. Effective utilization of any product is based on its quality, which, in turn, depends on the analytical data. The procedure described in this paper is the spectrophotometric method which meets most of the demands of analytical chemists namely; selectivity, sensitivity, simplicity, rapidity, reliability and cost of analysis. In this method, it is necessary to use iron (III) as the oxidizing agent; the use of such simple reagents makes the procedure cost-effective. One of the important facts is that this study will open up a new area of research Further value-addition to this method can be achieved, if the procedure is combined with on-line or at-line system and this is currently under investigation.

1. Introduction

Cardanol (3-pentadecenyl phenol) is a phenolic compound with Cis aliphatic chains in the meta position. It is a mixture of saturated and unsaturated (mono-, di- and tri-) compounds [1] commonly found in cashew nut shell liquid (CNSL), an alkyl phenolic oil which constitutes 25% of the total weight of cashew nut (Anacardium occidentale) a well-known species of the Anacardiaceae family [2]. CNSL is obtained as a by-product of cashew industry, and is an important source of unsaturated hydrocarbon phenol [3].

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Cardanol holds considerable promise because of its structural characteristics, [4], large availability in tropical areas, low cost and biodegradability [5]. The non-linear structure, unsaturation in the alkyl chain and substitution to phenolic group opens up new vistas in the innumerable applications in dyestuff, food, flavour, ion exchange resins, paints, plasticizers and polymers [6]. Significant studies have also been made in the technological application of cardanol and its derivative as pesticides [7] and surface-active agents [7] besides, in ceramics [4] and composites [5].

The phenomenal growth in the commercial applications of cardanol has encouraged the authors to develop sensitive, rapid and reliable methods for its determination. Survey of the literature revealed that no analytical method has been reported so far for its determination.

2. Objectives

The work described in this paper forms part of a systematic investigation to develop new spectrophotometric methods for agri products - a field of paramount importance due to easy biodegradability and use of agricultural waste and by-products, in place of toxic chemicals - an area of current interest in environmental management.

3. Methods

Apparatus

UV-VIS spectrophotometer UVIDEC-610 type with 1.0-cm matched cell (Jasco, Tokyo, Japan) was employed for measuring the absorbance values.

Reagents

Cardanol from Vittal Mallya Scientific Research Foundation, India, iron (III) chloride, (BDH, India), hydrochloric acid (Ranbaxy, India) was used. Alcohol was distilled before use and double distilled water was used throughout. Cardanol (100 mg) was dissolved in isopropyl alcohol in a 100-ml volumetric flask and made up to mark. This stock solution was diluted with isopropyl alcohol to get solutions of required strength. Aqueous solutions of 0.1% w/v iron (Ill) chloride containing few drops of 2N (v/v) hydrochloric acid and 0.1% w/v potassium ferricyanide was prepared in doubled distilled water.

Procedures

Aliquots of standard solutions of cardanol and 2.0 ml each of iron (III) chloride and potassium ferricyanide were taken in 25-ml calibrated flask. The contents were mixed well and kept aside for 20 min at room temperature. It was then diluted to 25-ml mark with distilled water and the absorbance was measured at 730 nm against the corresponding reagent blank and calibration graph was constructed. The optical characteristics for the determination of cardanol are shown in Table1.

Table 1: Spectral data for the determination of cardanol

Parameters	
Colour	Blue
λ_{max} (nm)	730
Stability (h)	2
Beer's law (ng ml^{-1})	2.0-15.0
Recommended drug concentration (µg ml^{-1})	5.0
Molar absorptivity (L mol^{-1} cm^{-1})	1.86 $x10^4$
Sandell's sensitivity (µg cm^{-2})	0.015
Regression equation*	
Slope (a)	0.1391
Intercept (b)	-0.004
Correlation coefficient	0.9982
R.S.D. %**	±1.02

*y=ax+b where x is the concentration of cardanol in µg ml^{-1}

** relative standard deviation(n=5)

4. Results and Discussion

The method is based on the reaction of cardanol with iron (III) salts in the presence of potassium ferricyanide in neutral medium to form a Prussian Blue (PB) product. The blue pigment iron (III) hexacyanoferrate (Il) has been produced for many decades to serve as a photostable material for making inks, paints, lacquers and the like [8]. In the recent past, other work describes, include, dopant in modified electrode [9] , composite films and code position of PB with polypyrrole [10]. Besides, PB has been extensively used as electrochemical sensor [11] , biosensor [12,13], ion sensor [14] and as chemical resistor for the determination of alkaline metals [15]. Spectral [16-21] and voltametric studies [22,23] give details of the structure, configuration and properties of PB which have been reported.

Addition of a few drops of 2N HCl is necessary to prevent precipitation of iron (III) as hydrated ferric oxide. Besides, the addition of hydrochloric acid will bring down the pH of the solution in slightly acidic range. Neutral ferric chloride free from hydrochloric acid is reported to give different colours, green, purple or blue which have been extensively exploited as a confirmatory test of phenols in organic chemistry [24]. The present work describes the details of the factors affecting the colour development, reproducibility, sensitivity and adherence to Beer's law.

5.

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Optimization of analytical variables

It was found that iron (III) chloride (0.1% w/v) in the range of 1.0-3.5 ml and potassium ferricyanide (0.1% w/v) in the range of 1.0-4.0 ml were necessary to achieve maximum colour intensity. Hence 2.0 ml each of iron (III) chloride and potassium ferricyanide solutions are recommended.

Order of addition

The order of addition of iron (III) chloride, ferricyanide and cardanol was studied via the formation of the blue complex. There was no appreciable change in the absorbance or colour of the product, when the order of addition of these reactants was varied.

Effect of solvents

The coloured product was developed at room temperature which was stable for 2 hours. Isopropyl alcohol was the preferred solvent for preparing stock solution of cardanol as ethyl alcohol and methyl alcohol interfered in the development of colour. Ethyl alcohol and methyl alcohol interfered only, if added before the development of the colour. Subsequently, both the solvents do not interfere in the reaction. Conversely, isopropyl alcohol can be used for dilution purposes. However, the use of isopropyl alcohol is discouraged, as it is more costly to ethyl alcohol and methyl alcohol. The solvents like DMF and DMSO were not chosen for the study because of their toxicity and high cost. Ethyl alcohol was preferred to methyl alcohol as it is nontoxic.

Calibration and spectral data

Molar absorptivity is an important parameter in UV-visible spectroscopic studies and it is a ratio of absorbance to concentration. Conversely, concentration is volume and molecular weight dependent.

The blue colour complexes obeyed Beer's law. The optical characteristics, such as optimum range, as evaluated from Ringbom plot, molar absorptivity, sandell's sensitivity, slope, intercept and correlation coefficient are shown in Table 1. The values indicate moderate dynamic range and high sensitivity.

Interference

The effect of various anions and cations on the determination of cardanol was studied as per the proposed procedures and the results are presented in Table 2 and 3. In general, 100 mg of the respective salt was added individually to aliquots containing 5.0 ug ml^{-1} of cardanol. The results showed that the methods are free from interference by any of the anions and cations, studied. However, cardol interfered in the determination.

Table 2: Effect of anion on the determination of cardanol

Salt of the anion added	Salt added mg	% Recovery of cardanol* ± RSD**
Ammonium phosphate	100	99.8 ± 0.71
Calcium carbonate	100	100.3 ± 0.98
Potassium bromate	100	99.9 ± 0.78
Potassium chloride	100	99.1 ± 0.61
Potassium iodate	100	99.0 ± 1.01
Potassium sulphate	100	98.4 ± 0.53
Sodium fluoride	100	98.9 ± 0.93
Sodium nitrate	100	99.6 ± 0.82
Sodium phosphate	100	100.3 ± 0.86
Sodium sulphate	100	99.5 ± 0.67

*5.0 µg ml^{-1} of cardanol

** relative standard deviation(n=5)

Table 3: Effect of cation on the determination of cardanol

Salt of the cation added	Salt added mg	% Recovery of cardanol* ± RSD**
Copper sulphate	100	100.2 ± 0.51
Barium sulphate	100	99.8 ± 0.99
Cadmium sulphate	100	98.7 ± 0.64
Lead nitrate	100	100.1 ± 0.89
Magnesium sulphate	100	100.4 ± 0.96
Manganese sulphate	100	98.7 ± 0.82
Potassium chromate	100	99.0 ± 0.62
Strontium nitrate	100	99.5 ± 1.04
Tin chloride	100	100.2 ± 0.67
Zinc sulphate	100	99.4 ± 0.61

*5.0 µg ml^{-1} of cardanol

** relative standard deviation(n=5)

Applications

Five crude samples of cardanol procured from different sources were analysed by the conventional standard addition method. Each sample was analysed with five

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replicates and the result of RSD was within 2%, and this margin of error is acceptable in all spectrophotometric determinations (Table 4).

Table 4: Cardanol content determined in various crude samples

SAMPLE	Amount of cardanol found by proposed method (g)	Cardanol added to the same sample (g)	Amount of cardanol found by difference (g)	Recovery **%
1	0.1080	0.100	0.1020	102.0
2	0.0995	0.100	0.0962	99.2
3	0.0993	0.100	0.0953	95.3
4	0.0984	0.100	0.1020	102.0
5	0.0162	0.100	0.0923	92.3

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