

LETTERS TO THE EDITOR

A QUICK METHOD OF DERIVING
WISHART'S DISTRIBUTION

THE joint probability differential of n independent observations on the p variates (X_1, X_2, \dots, X_p) distributed in the multivariate normal form with zero means and covariance matrix Σ is

$$(\text{Constant}) \cdot \exp\left(-\frac{1}{2} \text{tr } \Sigma^{-1} S\right) dX \quad (1)$$

where S is the $p \times p$ Wishart matrix

$$\sum_{i=1}^n (X_{i\alpha} X_{i\alpha}')$$

and dX is the volume element

$$\prod dX_{ij}, (i = 1, 2, \dots, p; j = 1, 2, \dots, n).$$

To obtain the distribution of S , integrate (1) in the domain S to $S + dS$, and in the process any function of S can be taken outside the integral sign leading up to

$$(\text{Constant}) \cdot \exp\left(-\frac{1}{2} \text{tr } \Sigma^{-1} S\right) \int_{S, S+dS} dX. \quad (2)$$

The integral, being a function of S , may be taken as $f(S) dS$, and therefore the distribution of S is

$$(\text{Constant}) \cdot \exp\left(-\frac{1}{2} \text{tr } \Sigma^{-1} S\right) f(S) dS. \quad (3)$$

It now remains to determine the nature of the function $f(S)$. To achieve this, introduce a transformation which takes over X to AX^* , the Jacobian of the transformation being $|A|^n$. Therefore

$$\begin{aligned} \int_{S, S+dS} dX &= \int_{S^*, S^*+dS^*} |A|^n dX^* \\ &= |A|^n f(S^*) dS^* \end{aligned} \quad (4)$$

where S^* stands for the Wishart matrix of X^* which are distributed as multivariate normal. Since $S = AS^*A'$, the function $f(S) dS$ could be transformed by this substitution, the Jacobian in this case being $|A|^{n+1}$. Therefore $f(S) dS \rightarrow |A|^{n+1} f(AS^*A') dS^*$. Identifying this with the last member of (4) we get

$$\frac{f(AS^*A')}{|AS^*A'|^{(n-p-1)/2}} = \frac{f(S^*)}{|S^*|^{(n-p-1)/2}}$$

showing that $f(S)/|S|^{(n-p-1)/2}$ is independent of the argument, and is therefore a constant.

This gives the nature of $f(S)$, and substituting this result in (3) the required distribution of S is obtained as

$$(\text{Constant}) \cdot \exp\left(-\frac{1}{2} \text{tr } \Sigma^{-1} S\right) |S|^{(n-p-1)/2} dS. \quad (5)$$

By using Siegel's lemma the value of the integral

$$\exp\left(-\frac{1}{2} \text{tr } \Sigma^{-1} S\right) |S|^{(n-p-1)/2} dS$$

is found (*vide* Cramer's *Mathematical Methods of Statistics*, p. 390) to be equal to

$$|\Sigma|^{n/2} 2^{np/2} \pi^{p(p-1)/4} \prod_{i=1}^p \Gamma\left(\frac{n-i+1}{2}\right)$$

and the constant in (5) is the reciprocal of this quantity.

This completes the proof of the derivation of Wishart's distribution.

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USE OF POTASSIUM THIOCARBONATE
(PTC) REAGENT IN THE
IDENTIFICATION OF COPPER (II)
AND CADMIUM (II) WHEN PRESENT
TOGETHER

POTASSIUM thiocarbonate has been earlier reported¹⁻⁶ as an efficient sulphide and thio-carbonate precipitant replacing the conventional use of gaseous hydrogen sulphide in the systematic cation groups separation involving common and less common metals. In the present communication, the soluble coloured complex formation property of PTC with certain d -transitional metals has been applied to the separation and identification of Copper (II) and Cadmium (II).

Despite the various available methods, detection of cadmium in the presence of copper is often attended with difficulty. However, the methods based on the complex cyanides of the two metals have found much favour. The complex, $[\text{Cd}(\text{CN})_4]^{2-}$ having relatively much higher instability constant (1.4×10^{-17}) than that (5.0×10^{-28}) of $[\text{Cu}(\text{CN})_4]^{3-}$ yields precipitates of $\text{Cd}(\text{OH})_2$ and CdS on treatment with formaldehyde⁷ and hydrogen sulphide^{8,9} respectively, leaving the copper cyanide-complex intact in solution. But requirement of control of soln. pH and the toxicity hazard of alkali cyanide restrict its use by a large group of students. Against this, the use of PTC offers safe and efficient analytical separation of the two metals irrespective of the quantities involved.

Procedure.—The solution, containing Cu^{2+} and Cd^{2+} , after the removal of other member-cations

of cadmium group, is taken in a centrifuge cone and made ammoniacal to yield $[\text{Cu}(\text{NH}_3)]^{2+}$ and $[\text{Cd}(\text{NH}_3)_4]^{2+}$. To this 0.5 M aq. soln. of K_2CS_3 is added dropwise. Initially, copper and cadmium are both precipitated as CuCS_3 (brown) and CdCS_3 (yellowish-orange) respectively. But on continued dropwise addition of K_2CS_3 soln. and warming at 60°C . by placing the cone in a water-bath, reddish coloured soluble complex, $\text{K}_2[\text{Cu}(\text{CS}_3)_2]$ is obtained, while the ppt. of CdCS_3 remains unaffected with excess K_2CS_3 . The two are separated by centrifuging. The centrifugate containing $\text{K}_2[\text{Cu}(\text{CS}_3)_2]$ is withdrawn and separately acidified with HCl to yield black ppt. of CuS on digestion on steam-bath. The treatment of the reddish centrifugate with HCl is an essential step for the confirmation of copper especially when it is present in relatively smaller amounts.

Modified Procedure in the Presence of Nickel and Cobalt.—Nickel (II) when treated with K_2CS_3 in ammoniacal medium yields initially a purple-red product, $[\text{Ni}(\text{NH}_3)_4]\text{CS}_3$, which with excess of the thiocarbonate reagent results in forming the blood-red complex, $\text{K}_2[\text{Ni}(\text{CS}_3)_2]$. Cobalt (II) under similar conditions forms the brownish-black complex, $\text{K}_2[\text{Co}(\text{CS}_3)_2]$. As such, in the presence of nickel or cobalt, the centrifugate after separation from CdCS_3 would be intense red, or brownish thereby masking the reddish colour due to copper when present. However, the intense coloured nickel and cobalt complexes are easily decomposed with a few drops of H_2O_2 on heating whereas the copper complex, $\text{K}_2[\text{Cu}(\text{CS}_3)_2]$, yields brown ppt. of $\text{CuO}\cdot\text{XH}_2\text{O}$. Alternatively, on treatment of the nickel or cobalt complex with dil. HCl no ppt. is produced as against a black ppt. obtained from the copper complex.

Cation Generation Technique for the Identification of Cu (II) and Cd (II) at Semi-micro scale.—The chelates of copper and cadmium with Trilon B (di-sod. EDTA) on gradual treatment with 0.5 M aqueous PTC result in the gradual development of red colour due to copper and a compact orange-coloured ppt. of CdCS_3 from ammoniacal solutions. Corresponding chelates of Ni (II) and Co (II) are masked against PTC and hence create no interference.

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LUTEOLIN AS A CHARACTERISTIC FLAVONE OF ACANTHACEAE

In recent years plant phenolics and their glycosides have assumed some importance from the point of view of biochemical systematics¹ and the usefulness of chemistry in plant taxonomy as illustrated by the flavonoid constituents has also been discussed.² Myricetin has been recorded as a characteristic flavonol of *Hamelidaceae* and *Anacardiaceae*³ and arbutin and hydroquinone of *Proteaceae* and possibly *Pyrolaceae*.⁴ Since the members of the *Acanthaceae* family do not seem to have been studied in any detail for their flavonoids, we have chemically examined eleven members of this family growing in and around Pondicherry for their flavonoids and our results are summarised in Table I.

TABLE I

Plant	Part examined	Flavone
1. <i>Rungia repens</i>	Flowers and leaves	Luteolin
2. <i>Thunbergia grandiflora</i>	"	"
3. <i>Adhatoda vasica</i>	"	"
4. <i>Asteracantha longifolia</i>	"	"
5. <i>Ruellia tuberosa</i>	"	"
6. <i>Barleria strigosa</i>	"	"
7. <i>B. cristata</i>	"	"
8. <i>Justicia gendarussa</i>	"	"
9. <i>J. pr. strata</i>	"	"
10. <i>Andrographis paniculata</i>	Leaves	"
11. <i>Thunbergia erecta</i>	"	"

Luteolin has been isolated and identified from the flowers of *Rungia repens*,⁵ *Thunbergia grandiflora* and *Adathoda vasica* and in others the occurrence of the flavone established by means of paper chromatography and comparison with an authentic sample of the pigment. The flowers of *T. grandiflora* have been found to contain appreciable amounts of iron also.