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Fluorescence sensing and intracellular imaging of Pd^{2+} ions by a novel coumarinyl-rhodamine Schiff base†

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Coumarinyl-rhodamine, **HCR**, served as an extremely selective sensor for Pd^{2+} ions in ethanol/H_2O (8 : 2, v/v, HEPES buffer, pH 7.2) solution and the limit of detection (LOD) was 18.8 nM (3σ method). The free sensor, **HCR**, was weakly emissive and in the presence of Pd^{2+}, the colour changed from straw to pink with very strong emission at 598 nm in the presence of eighteen other cations. A plausible mechanism involved opening of the spirolactam ring of rhodamine on interaction with Pd^{2+}, which was justified by structure optimization and transition energy calculations using the DFT technique. **HCR** underwent 1 : 1 complexation with Pd^{2+}, which was confirmed *via* the Job's plot, mass spectra and Benesi–Hildebrand plot (association constant K_a, 9.1 × 10^4 M^{-1}). A separate *in vitro* experiment showed that **HCR** could specifically sense Pd^{2+} in MCF7 (human breast adenocarcinoma) cell lines.

1. Introduction

In the last few years, the development of methods for the identification and sensing of platinum group metals (PGMs) has received considerable interest because of their enormous biological, environmental, industrial and chemical significance.[1–4] Among these, palladium, a precious metal, has become one of the most attractive sensing targets in recent years because of its wide catalytic use in the synthesis of organic and pharmaceutical molecules, fuel cells, dental appliances, medical devices, electrical equipments, *etc.*[5,6] In the Pd-catalysed reactions, either the Pd(0) may be temporarily oxidized or Pd(IV) may be reduced to Pd(II) during the reactions. The final product is often contaminated with a Pd(II) impurity even after rigorous purification. Such contamination at an ultratrace level in industrial products may cause serious health problems. Due to its thiophilic nature, palladium can bind with DNA, proteins and other macromolecules and disturb a variety of cellular processes.[7,8] Moreover, palladium also hinders the activity of many enzymatic reactions such as those of alkaline phosphatase, creatine kinase and prolyl hydroxylase (hypoxia-inducible factor).[9,10] Therefore, various analytical techniques are used for the quantitative analysis of palladium. Popular techniques include inductively coupled plasma-mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS), solid-phase microextraction high performance liquid chromatography (SPME-HPLC) and X-ray fluorescence spectroscopy.[11–13] However, these methods require sophisticated highly expensive equipments, extensive sample preparation steps, and time-consuming and high salaried experts. Among these different techniques used for the analysis of palladium ions, colorimetric and fluorometric techniques are more convenient and dependable for the rapid and sensitive detection of palladium both qualitatively and quantitatively because of their simplicity, selectivity and sensitivity. Hence, the development of palladium-selective fluorescent probes is extremely essential. Pd^{2+}, being a heavy transition metal ion with open shell electronic configuration, is a typical fluorescence quencher.[14] Based on the ON–OFF[15] or OFF–ON[16,17] mechanism, some fluorescent chemosensors and chemodosimeters are synthesized for identifying palladium species. For the design of a sensor, the important objectives are long-wavelength emission and ecofriendly availability of fluorescent chemosensors. Thus, rhodamine-functionalized chemosensors are receiving considerable interest in current years.[18] For the last couple of years, we have considered a strategy to design rhodamine derivatives for the identification of trace levels of Pd; allyl ether Schiff base of rhodamine[19] was tested for the detection of total Pd at 50 nM, while allyl ether hydrazone rhodamine could detect as low as 95 nM concentration[20] at pH 7.2. The performance of rhodamine derivatives inspired us to synthesize newer

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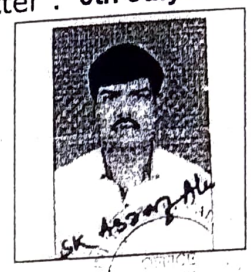
Date of Enrollment : **5th June 2018**
Registration Number : **04630/Ph.D.(Sc.)Proceed/2019**
Date of Registration : **4th July 2019**
(Please quote the above Number and Date in all future Correspondence)

Date of Letter : **5th July 2019**



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Dear Sir,

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Name of the Supervisor : **Dr. Mijanur Rahaman Molla**
Name of the Joint Supervisor : **Dr. Shubhankar Samanta** ✓
Name of the Associate Supervisor : **X**

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TO WHOM IT MAY CONCERN

This is to certify that the thesis entitled ***"Environmentally benign synthetic routes to fused heterocycles and their photophysical studies"***, submitted by **Mr. Anirban Bera** who got his name registered on 12-10-2018 (**Index No.- 235/18/Chem./26**) for the award of Ph.D. (Science) degree, Jadavpur University, is absolutely based upon his own research work under our supervision and that neither this thesis nor any part of it has been submitted for either any degree or diploma or other academic award anywhere else before.

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28.06.2023
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ANNEXURE : 1.2

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A new integrated likelihood for estimating population size in dependent dual-record system

Kiranmoy CHATTERJEE[1] and Diganta MUKHERJEE[2]

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Key words and phrases: Capture–recapture; direction of behavioural dependence; human population; nuisance parameter; time-behavioural response variation model.

MSC 2010: Primary 62F10, 92K80; secondary 62J99, 62P10.

Abstract: Efficient estimation of the population size from dependent dual-record system (DRS) remains a statistical challenge in the capture-recapture type experiment. Owing to the non-identifiability of the suitable time-behavioural response variation model (denoted as M_{tb}) under DRS, few methods are developed in the Bayesian paradigm based on informative priors. Our contribution in this article is to develop a new integrated likelihood function from model M_{tb} motivated by a novel approach developed by Severini (2007). A suitable weight function on the nuisance parameter is derived with the knowledge of the direction of behavioural dependency. A pseudo-likelihood function is constructed so that the resulting estimator possess some desirable properties including negligible prior (or weight) sensitiveness. Extensive simulations show the superior performance of our proposed method to that of the existing Bayesian methods. Moreover, the proposed estimator is easy to implement from the computational perspective. Applications to two real data sets are presented. *The Canadian Journal of Statistics* 46: 577–592; 2018 © 2018 Statistical Society of Canada

Resumé: L'estimation efficace de la taille d'une population à partir d'un système à enregistrement double (SED) dépendant demeure un défi statistique de taille pour les expériences de type capture-recapture. Peu de méthodes ont été développées dans un cadre bayésien avec des lois a priori informatives, surtout à cause de la non-identifiabilité du modèle pour la variation temporelle du comportement (dénoté M_{tb}) avec un SED. Les auteurs développent une nouvelle fonction de vraisemblance intégrée à partir du modèle M_{tb} motivée par une approche novatrice proposée par Severini (2007). Ils dérivent une fonction de pondération appropriée pour les paramètres de nuisance avec la connaissance de la direction de la variation temporelle du comportement. Ils construisent une fonction de pseudo vraisemblance conférant à l'estimateur obtenu des propriétés désirables, notamment une sensibilité négligeable à la loi a priori et à la pondération. De plus, l'estimateur proposé est facile à implémenter d'un point de vue numérique. Les auteurs présentent une vaste étude de simulation démontrant les performances supérieures offertes par la méthode proposée par rapport aux méthodes bayésiennes existantes. Ils en présentent également l'application à deux jeux de données réelles. *La revue canadienne de statistique* 46: 577–592; 2018 © 2018 Société statistique du Canada

1. INTRODUCTION

The dual-record system (DRS) is a special type of capture–recapture experiment, which is particularly designed for estimating the size of a specified population, say N, based on two

Additional Supporting Information may be found in the online version of this article at the publisher's website.

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OLS: Is That So Useless for Regression with Categorical Data?

Atanu Biswas, Samarjit Das and Soumyadeep Das

Abstract Binary/categorical response data abound in many application areas poses a unique problem; OLS-based model may lead to negative estimate for probability of a particular category and does not provide coherent forecast for the response variable. This unique and undesirable property of linear regression with categorical data impedes the use of OLS which otherwise is the simplest and distributionally robust method. The logit or probit kind of solution is heavily distribution dependent or link function dependent. Failure of such distributional assumption of the underlying latent variable model may cost the estimators heavily and may lead to biased and inconsistent estimates, in general. In this paper, we attempt to fix the inherent problem of linear regression by suggesting a simple manipulation which, in turn, leads to consistent estimates of probability of a category, and results in coherent forecasts for the response variable. We show that the proposed solution provides comparable estimates, and sometimes, with respect to some criterion, the proposed method is even slightly better than the logit kind of models. Here, we consider different underlying error distributions and compare the performances of the two models (in terms of their respective residual sum of squares and also in terms of relative entropy) based on simulated data. It is evidenced that the OLS performs better for many distributions, viz., Gamma, Laplace, and Uniform error distributions.

Keywords Logit model · Ordinary least square · Residual sum of squares Relative entropy

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A. K. Laha (ed.), *Advances in Analytics and Applications*, Springer Proceedings in Business and Economics, https://doi.org/10.1007/978-981-13-1208-3_18

ANNEXURE : I.5

JOURNAL OF STATISTICAL COMPUTATION AND SIMULATION
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Nonparametric approaches for comparing three-period, two-treatment, four-sequence crossover designs

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BSTRACT

he paper describes nonparametric approaches for comparing ree-period, two-treatment, four-sequence crossover designs rough testing the hypothesis that the treatments are interchange- ble. The proposed approaches are based on a model which incor- orates, along with the direct treatment effects, self and mixed car- yover effects. Related asymptotic results are obtained. Comparisons among the designs are made numerically with respect to type I error rate and power of the tests considering compound symmetry and autoregressive covariance structures of the response variables. Lengths of the confidence intervals of the treatment differences are also used to make comparative study among the designs.

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Asymptotic distribution; asymptotically distribution-free; Balaam's design; crossover design; mixed carryover effect; self carryover effect; step-down approach

1. Introduction

In clinical research, where two or more treatments are under comparison, patients receive treatments in groups. Here it is important that single measurement from each patient is not appropriate in the statistical sense and it may produce bias due to his/her initial condition. This emerges the concept of repeated measurement studies by which subjects are given treatments more than once over time. Crossover and parallel group trials produce such studies in practice. In particular, when disease under study is chronic and stable (e.g., cancer, arthritis, obesity, asthma), clinical researchers are inclined to crossover trials as they possess certain medical ethics.

In crossover design with more than two periods, there should be a restriction to those designs in which the first two periods represent one of the basic crossover designs. Thus, for comparing two treatments, denoted by A and B, through crossover design, the first two periods should be $\{AB, BA\}$ (usual crossover design) or $\{AA, AB, BA, BB\}$ (Balaam's design). See, for example [1–3]. This is because of the fact that, if the extra treatment periods result in an excessive number of withdrawals, it will still be possible to carryout analysis with the first two periods in the usual way [4]. This leads us an approach to get a three-period design with a view to achieve higher efficiency than the corresponding two-period crossover design.

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Ref. .No: D-7/Sc/1365/16

Dated : 09. 11. 2016.

To,
Smt. Nibedeeta Rani Sarraf
C/O.: – Prof. Parimal Karmakar
Head
Dept. of Life Sc. & Bio-technology
Jadavpur University
Kolkata-700032.

INDEX No: 221/16/Life Sc./25

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