# ISOLATION AND IDENTIFICATION OF TOXIC CHLORINATED ORGANIC COMPOUNDS PRESENT IN BLACK LIQUOR OF BLEACHED CELLULOSE PULP FROM SOUTHERN BRAZIL

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*Abstract. Chemical components of untreated black liquor of cellulose pulp from Southern Brazil were extracted using macromolecular XAD-4 resin. The following compounds were identified qualitatively and/or quantitatively by capillary gas chromatography: phenol; guaiacol; catechol; 3,4-dichlorocatechol; 3,4,5-trichloroguaiacol; 4,5,6-trichloroguaiacol; 3,4,5-trichlorocatechol; pentachlorophenol; tetrachloroguaiacol; trichlorosyringol and tetrachlorocatechol. The retention indexes of some of these toxic and mutagenic compounds were also determined.*

The study and control of effluents from the pulp and paper industry has been the subject of considerable research efforts during the last decade.[1-5] Bleach plant effluents, or black liquor, contains a broad spectrum of organic substances, in most cases degradation products of lignin and cellulose. Since chlorine or hypochlorite are used as bleaching agents chlorinated organic compounds, particularly phenols and their derivatives, are commonly present in black liquor. Most of them, besides being mutagenic are highly toxic to the aquatic flora and fauna.[6-12]

The present communication deals with extraction, identification and determination of retention indices of various chlorinated phenols, guaiacols and catechols present in untreated black liquor of cellulose pulp from Southern Brazil. The samples of effluents were obtained from paper mills using mixtures of hardwood (eucalyptus) and softwood (pine) subjected to Kraft treatment. The extraction was performed using crosslinked polystyrene macroreticular resin (Amberlite XAD-4) supplied by Rohm and Haas, Philadelphia, Pennsylvania, USA, following the procedure described in the literature.[11] The elution from resin columns was done with diethyl ether/methanol (10:1) and the concentrated extract (5ml from 10 l of black liquor) was analyzed by capillary gas chromatography using a CG 3537D chromatograph manufactured by Instrumentos Científicos CG Ltda., São Paulo, Brazil, equipped with an injection system for capillary columns, flame ionization detector and linear temperature programming. The chromatograms were obtained with a HCG recorder (Instrumentos Científicos CG Ltda) and the retention times and the peak areas were determined with a CDS 111 integrator-processor (Varian Indústria e Comércio Ltda., São Paulo). A SE-30 fused silica capillary column with a film thickness od 0,25 μM made by J&W Scientific, Inc., Rancho Cordova, California, USA, was employed. The identification of all of the compounds was performed in conjunction with known standards. The retention times were not used for identification. Figure 1 illustrates a typical chromatogram obtained for samples of untreated black liquor indicating the components that have been identified.

The quantitative determination was obtained by comparison of areas or peak heights of standards of known concentration in chromatograms containing the standards alone, the standards with the sample and the sample alone. A summary of the experimental results determined is given in Table I. In general, it can be said that the concentrations determined are comparable to those reported in the literature, mostly for softwoods.[4,6,10,13,14] The higher values obtained for trichlorosyringol may be explained in terms of the nature of the pulp. According to the literature, this compound is found in higher concentration in effluents originating from hard-

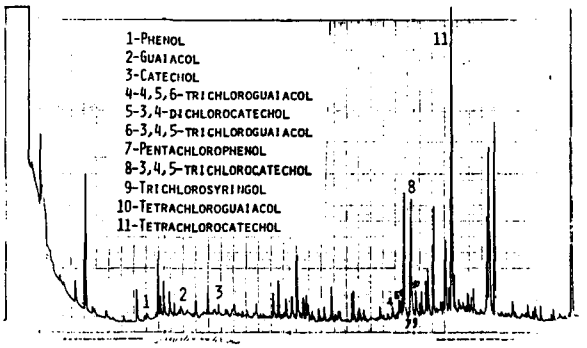


FIGURE 1. GAS CHROMATOGRAM OF UNTREATED BLACK LIQUOR EXTRACT (60m SE-30 column, Progr. 4°C/min, $T_{col}$=25-300°C, Vol. inj. 1 µl, splitless) INDICATING SOME OF THE IDENTIFIED COMOPNENTS.

woods.[10] The higher concentrations of tetrachlorocatechol and pentachlorophenol are open to question. Based on the values obtained it may be concluded that the untreated effluent is highly toxic since the median lethal concentrations for 96 hours (96-hr-LC50) for some of the compounds have been surpassed and the cumulative effect of all of them is not even being considered.[4]

TABLE I. CONCENTRATION OF SOME OF THE COMPOUNDS IDENTIFIED IN UNTREATED BLACK LIQUOR

| Compound | Concentration ( µg/l ) Found* | Literature** |
|---|---|---|
| Trichlorosyringol | 173 | 0- 140 |
| 3,4-Dichlorocatechol | 288 | 50- 520 |
| 3,4,5-Trichlorocatechol | 5885 | 350-15000 |
| Tetrachlorocatechol | 16461 | 300- 5300 |
| 4,5,6-Trichloroguaiacol | 500 | 300- 1500 |
| Tetrachloroguaiacol | 423 | 50- 1200 |
| Pentachlorophenol | 21 | 0.2 |

* The minimum detectable quantity ranged from 0.003 ug/l for trichlorosyringol to 0.021 µg/l for tetrachloroguaiacol.
** References 4,6,10,13,14.

The retention indexes (Kovats indexes,I) of some of the chlorinated compounds were determined according to the method proposed by Guiochon.[15] Tis involved the use of hydrocarbon standards ranging from 6 to 25 C atoms and linear temperature programming (6°C/min) in the 25°-300°C range. The average values obtained for the retention index (I) are summarized in Table II.

TABLE II. RETENTION INDEXES DETERMINED FOR SOME OF THE CHLORINATED COMPOUNDS

| | |
|---|---|
| Phenol | 935 |
| Guaiacol | 993 |
| Catechol | 1192 |
| 4,5,6-Trichloroguaiacol | 1625 |
| 3,4-Dichlorocatechol | 1668 |
| 3,4,5-Trichloroguaiacol | 1693 |
| Pentachlorophenol | 1730 |
| 3,4,5-Trichlorocatechol | 1752 |
| Trichlorosyringol | 1764 |
| Tetrachloroguaiacol | 1769 |
| Tetrachlorocatechol | 1908 |

Korhonen reported a value of 940 for phenol and 1725 for pentachlorophenol as part of a study of chlorobenzenes, chlorobenzaldehydes and related compounds.[16] In general, the addition of a Cl substituent causes an increase in the value of the retention index. The substituent effect is however not simply additive and depends on the position on the ring and the number of chlorine atoms. The retention indices are useful as an analytical parameter and may also be used to predict physical and chemical properties.

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## UM NOVO MÉTODO DE DESACETILAÇÃO EM QUÍMICA DE CARBOIDRATOS

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Abstract: A NEW METHOD FOR DEACETYLATION IN CARBOHYDRATE CHEMISTRY

The carbohydrate acetates, easily purified and interconvertible with the parent substances, are ideal derivatives in carbohydrate chemistry. Deacetylation is carried out by methanolic solution containing sodium methoxide or ammonia.

We report in this note a new method for deacetylation by the use of uranyl acetate.

Introdução:

Os ésteres são os derivados mais comumente utilizados em química de carboidratos, pois são produtos frequente - mente cristalinos e de fácil purificação. Estes derivados são também importantes produtos de partida na síntese de oligossacárides [1,2].

Os métodos disponíveis para a remoção destes grupos empregam solução metanólica de metóxido de sódio[4,7] ou de amônia[8]. Um acompanhamento cuidadoso do desenvolvi - mento da reação é necessário quando estão presentes, na molécula, grupos sensíveis à base.

A técnica que emprega solução metanólica de acetato de uranila, desenvolvida em nosso laboratório, permite, em condições suaves, a remoção de grupos acetato em bom rendimento.

Procedimento Geral:

As soluções dos monossacárides I, II e do dissacáride III ( 0,7mM ) em metanol ( 25ml ) adicionou-se acetato de uranila ( 1,2 mEq ) e as misturas foram deixadas, sob agitação, à temperatura ambiente durante duas horas. Após este tempo, cromatografia em camada delgada de sílica (n-butanol, acetona, água 4:5:3, v/v) tendo como revelador etanol/$H_2SO_4$ a 5%, mostrou