Disciplina de Tecnologia de Pós-colheita e Industrialização de Arroz

Cromatografia aplicada a determinação de qualidade de arroz

Dra. Shanise Lisie Mello El Halal

O que é qualidade?

"Qualidade é o grau em que um produto atinge ou excede as expectativas do consumidor"

Fonte: FAO – Food Safety and Quality in Europe (2004).

Visão geral dos componentes em alimentos

Componentes voláteis	Não voláteis e semi voláteis	Outros
• Sabor e fragrância • Sabores indesejáveis	• Lipídeos • Proteínas • Carboidratos • Carotenoides • Vitaminas • Antioxidantes • Polifenóis....	• Agrotóxicos • Medicamentos veterinário • Micotoxinas • Contaminantes - como metais • Migrantes de material de embalagens • Resíduos de processo e/ou armazenamento

Determinação de compostos orgânicos em alimentos

Extração com solventes orgânicos

↓

Separação, identificação e quantificação → cromatografia

↓

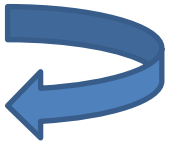
- Cromatografia de camada delgada
- Cromatografia líquida de alta eficiência
- Cromatografia gasosa

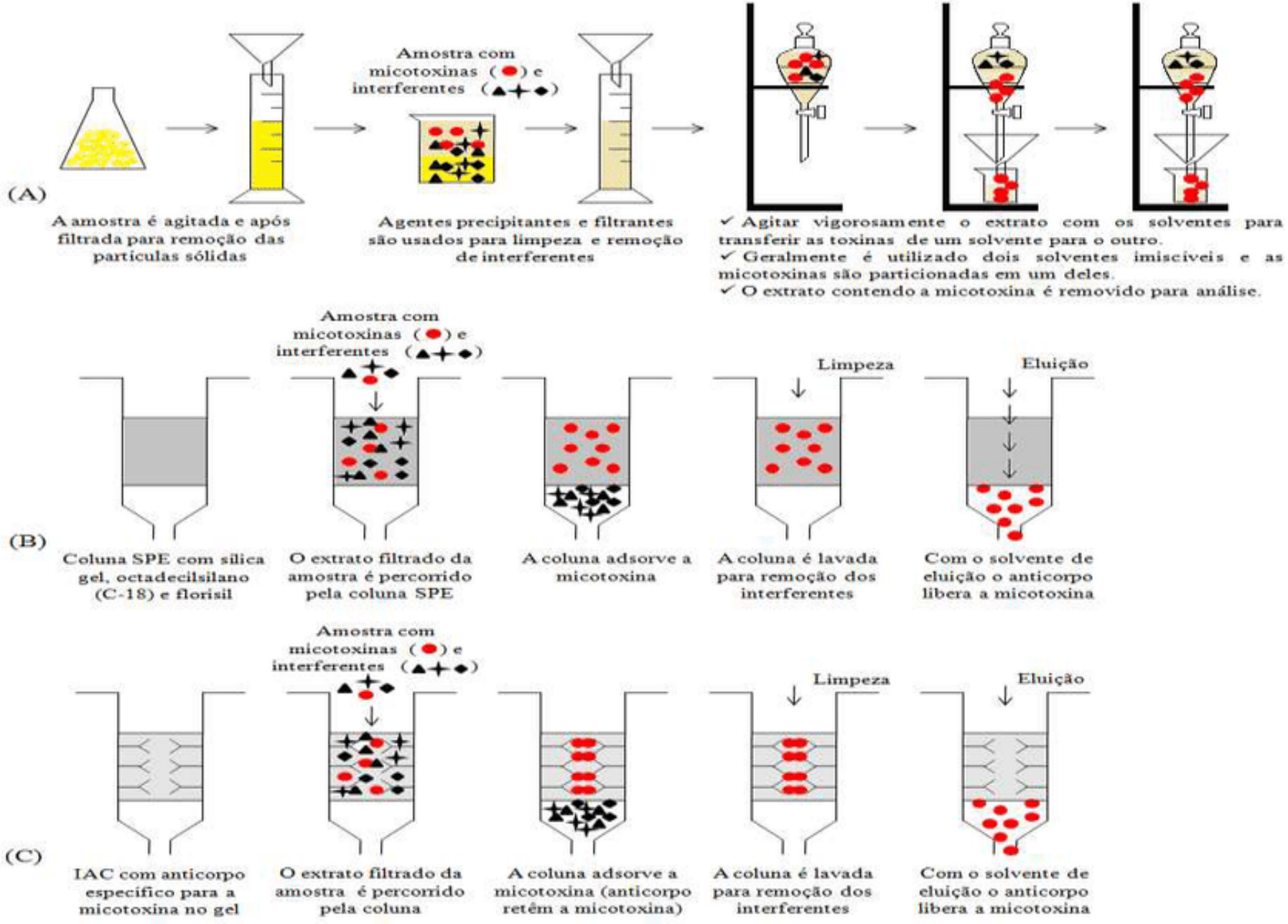
Principais técnicas de extração

- ✓*Extração Líquido-Líquido*
- ✓*Extração em Fase Sólida (SPE)*
- ✓*Microextração em fase sólida - Voláteis*
- ✓*Coluna de iminoafinidade – Micotoxinas*
- ✓QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe)

(Rápido, Fácil, Barato, eficaz, robusto, seguro

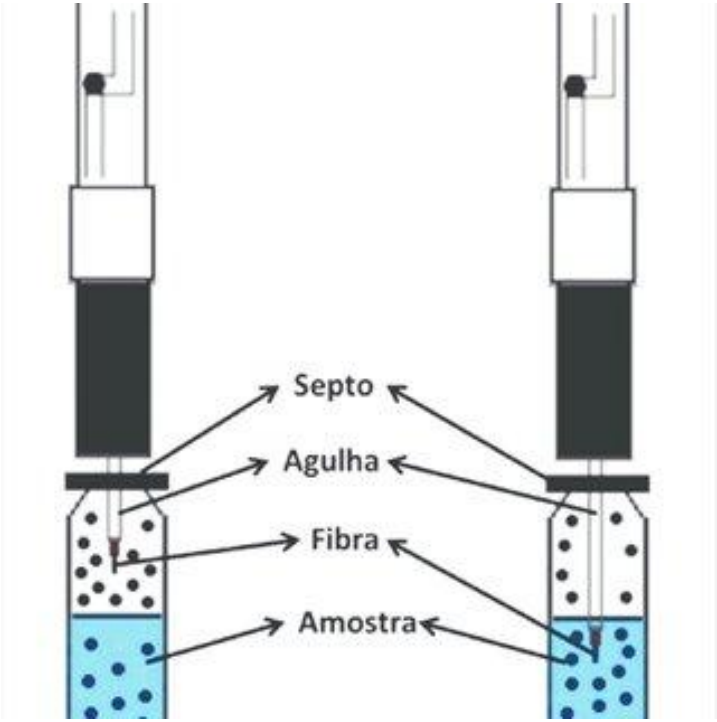
Multiresíduos de agrotóxicos e micotoxinas





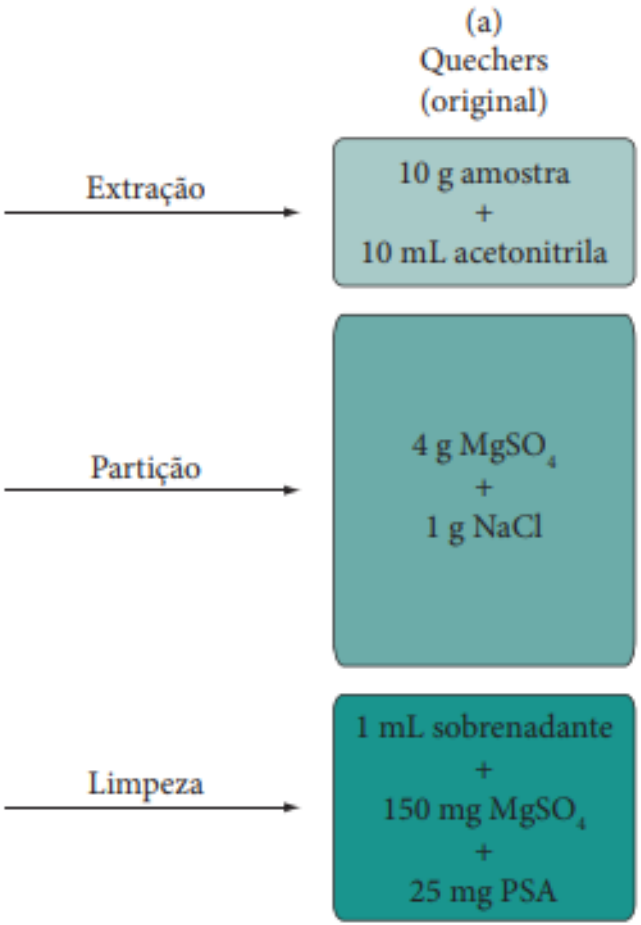
Procedimentos de purificação do extrato da amostra comumente utilizados para análise em alimentos. (A) extração líquido-líquido (LLE), (B) extração em fase sólida (SPE) e (C) coluna de imunoafinidade (IAC).

Extração a partir da técnica Microextração em fase sólida



Muito usada para compostos voláteis

Extração a partir da técnica QuEChERS



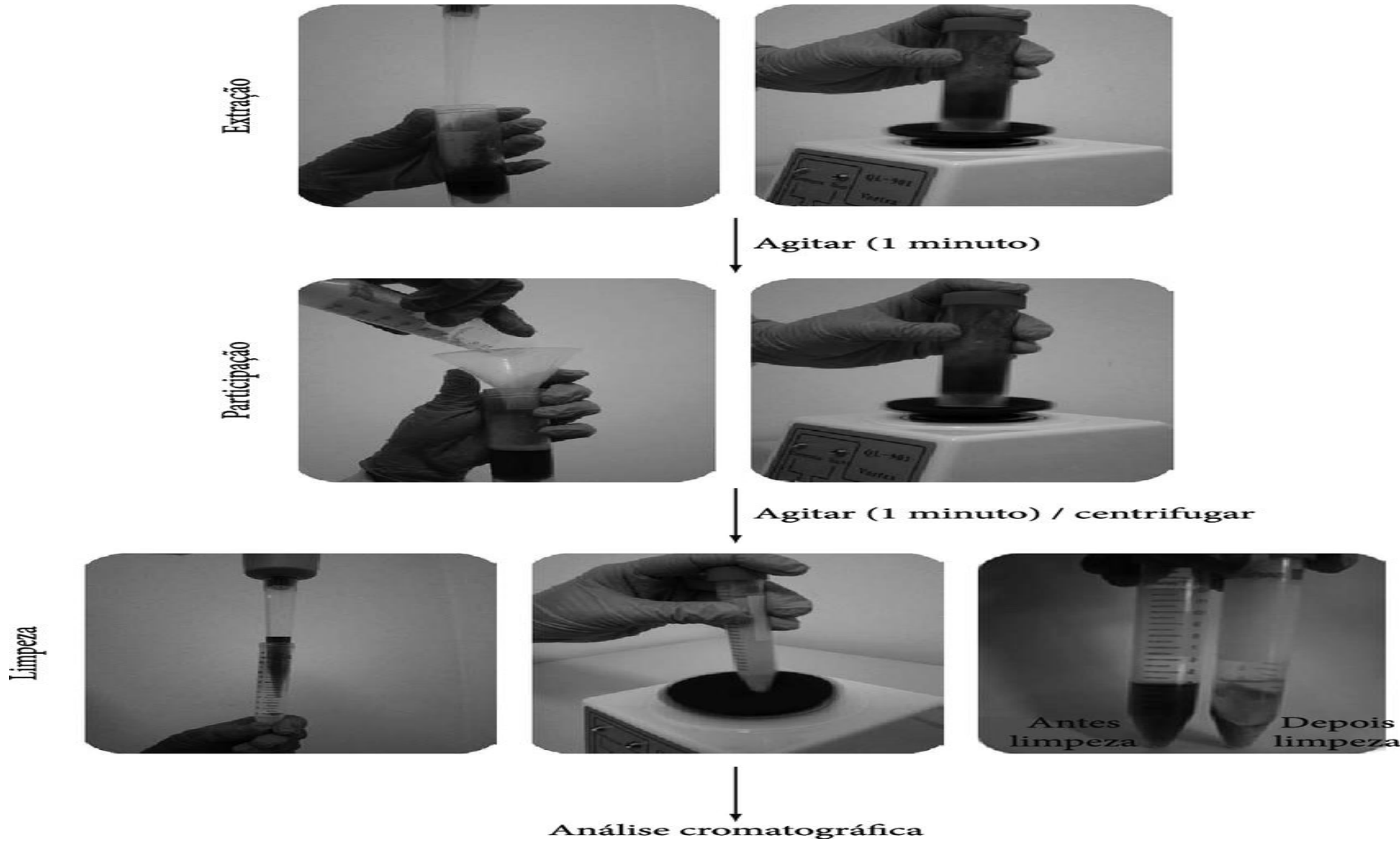
Acetonitrila = extrai ampla faixa de agrotóxico
Menor extração de interferentes lipofílicos

Sal diminui solubilidade dos componentes polares, aumentando sua recuperação.

PSA (AMINA PRIMARIA SECUNDÁRIA)
Sorvente que remove interferentes da matriz

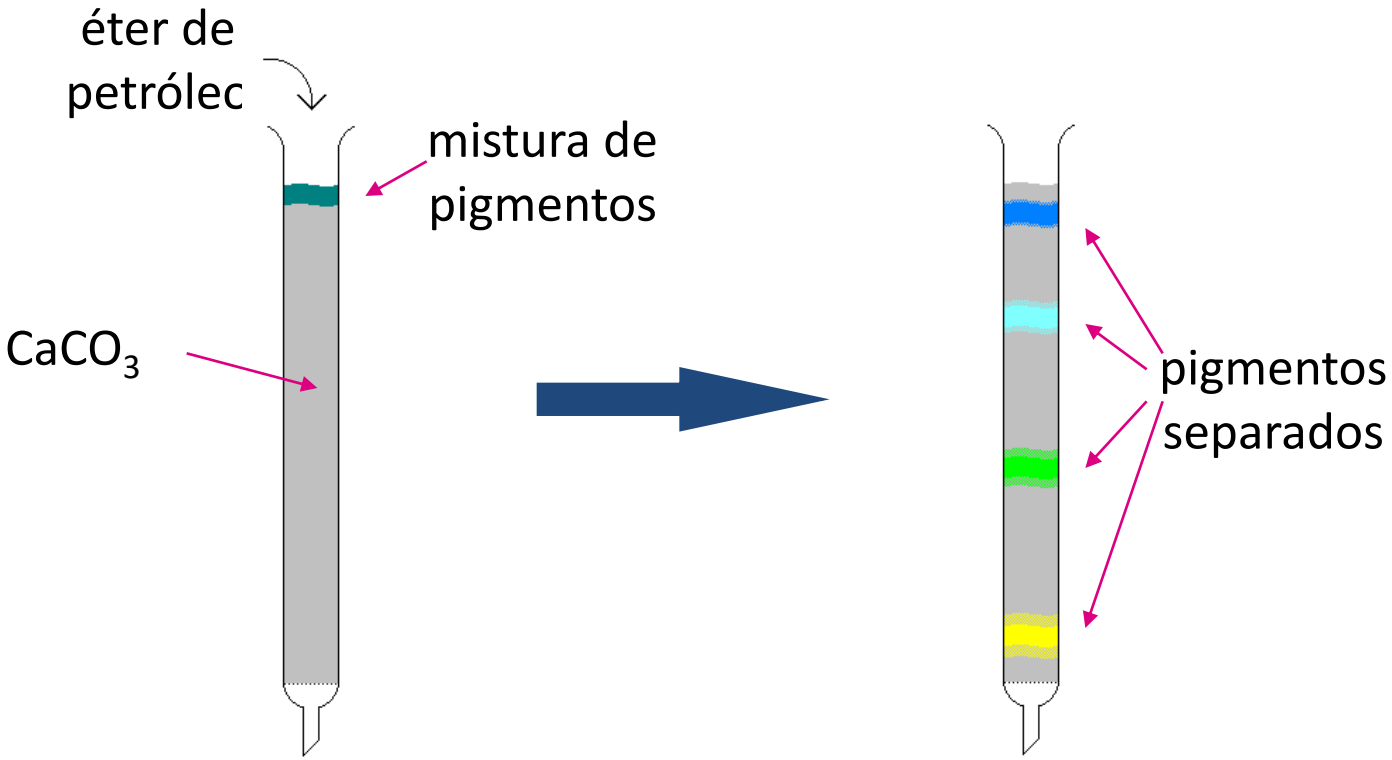
Açucares , ácidos graxos, ácidos orgânicos, pigmentos.

Extração a partir da técnica QuEChERS



Histórico da Cromatografia

Mikhail (Michael, Mikhael) Semenovich Tswett (1903), botânico russo: Separação de misturas de pigmentos vegetais em colunas recheadas com adsorventes sólidos e solventes variados.



1906 → Cromatografia = *chroma* [cor] + *graphe* [escrever] (grego)

Definição de cromatografia

Método de separação no qual a amostra sofre um processo de partição entre duas fases: uma permanece imóvel **(estacionária)** e a outra percola através dela **(móvel)**.

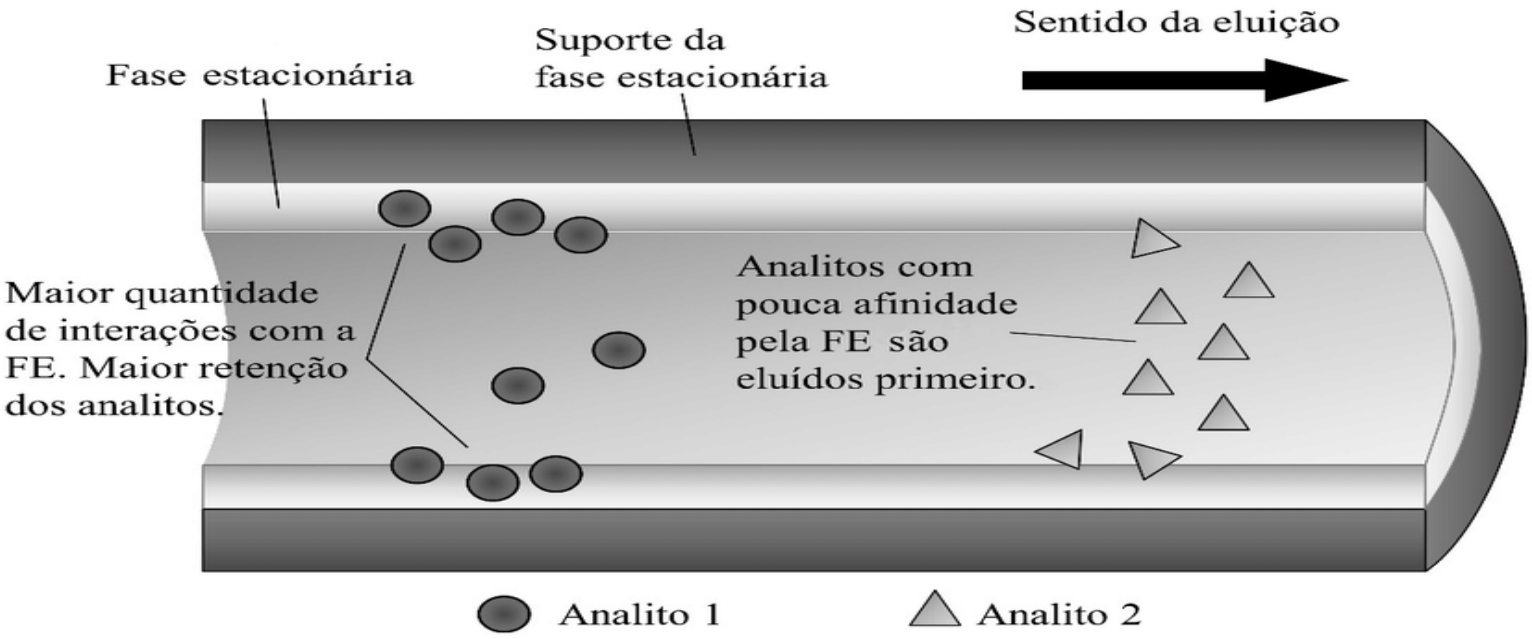


Figura 1. Esquema simplificado de separação de duas misturas.

Definição de cromatografia

Analogia

O processo cromatográfico pode ser comparado a um grupo de abelhas e moscas sobrevoando uma certa região.Ao passarem por uma flor, espera-se algum efeito sobre as moscas e abelhas.

Fase estacionária

Analitos

Definição de cromatografia

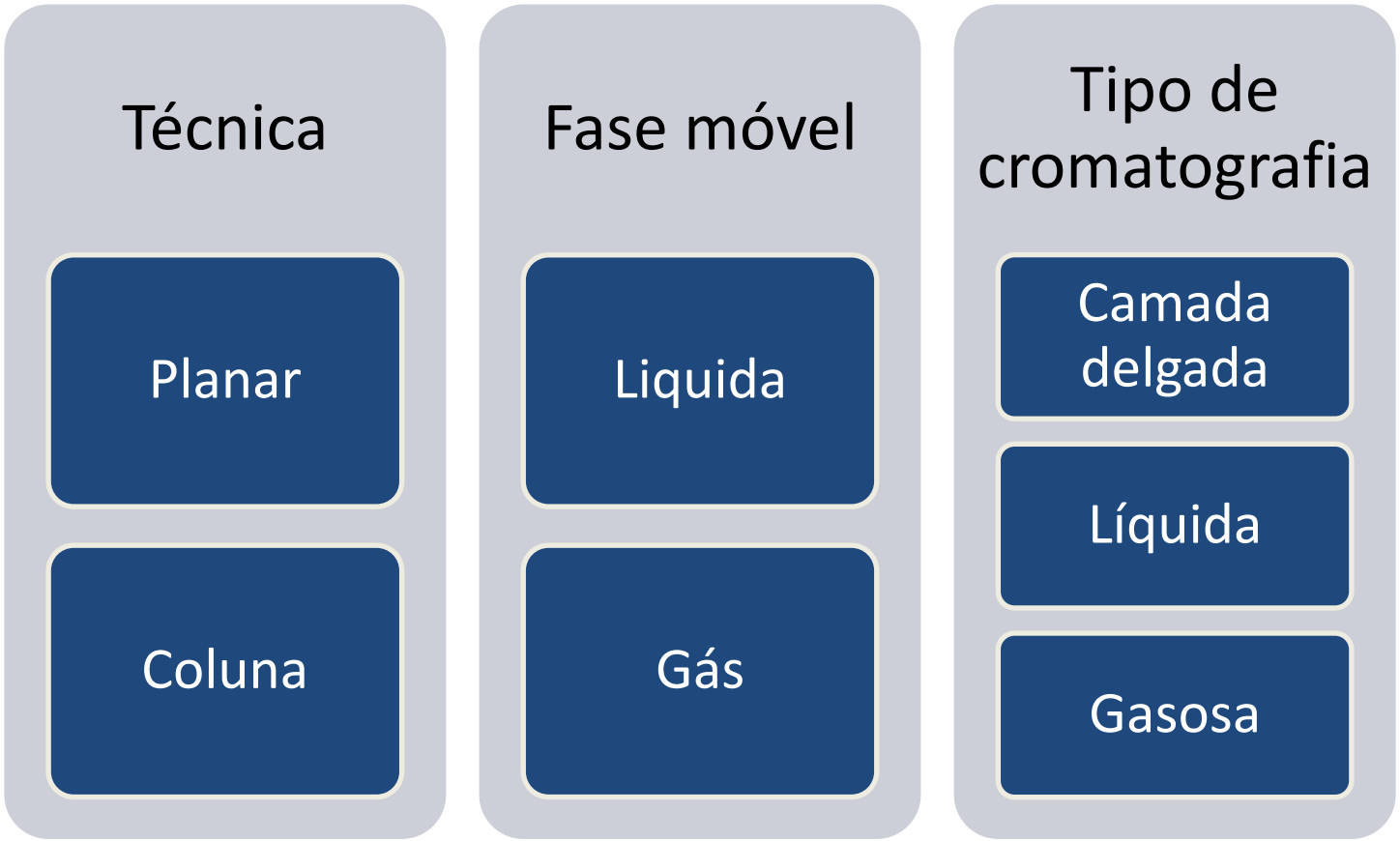
Analogia

Para uma mesma mistura, a simples troca da fase estacionária pode ser suficiente para alterar completamente a ordem de eluição de componentes da mistura.

Fase estacionária

Analitos

Classificação



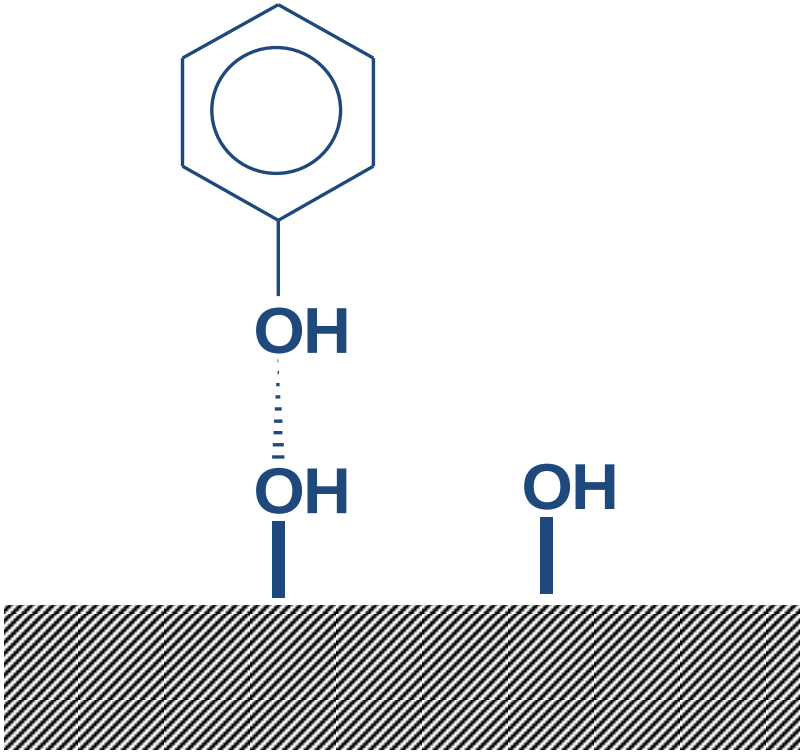
Mecanismo de separação

- **Adsorção**
- **Absorção (Partição)**
- **Troca iônica**
- **Exclusão**

Mecanismo de separação

Adsorção

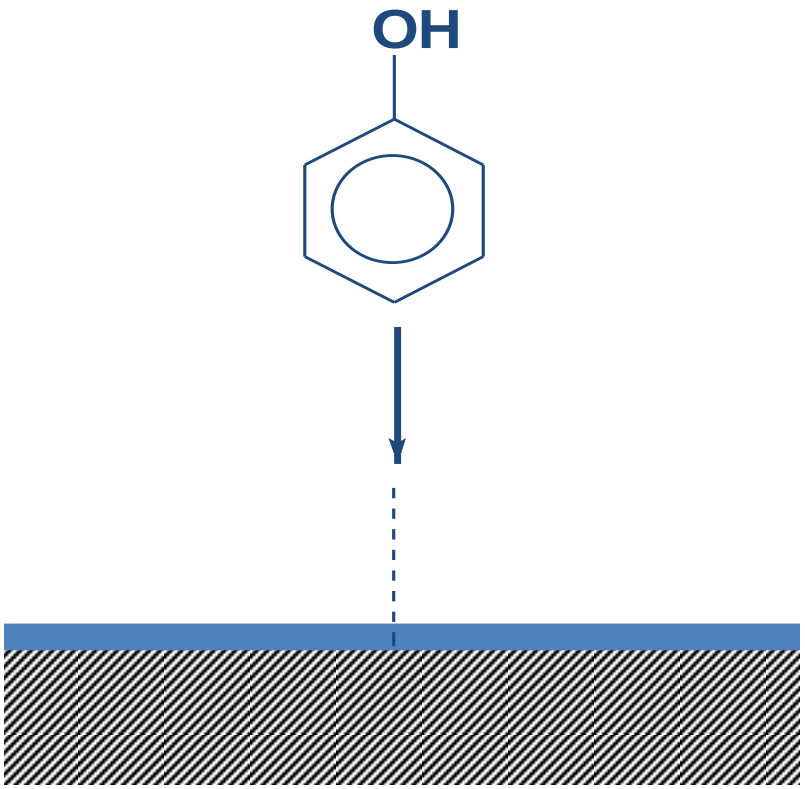
A adsorção ocorre entre a interface entre o sólido e a fase móvel, devido aos grupos ativos da superfície.



Mecanismo de separação

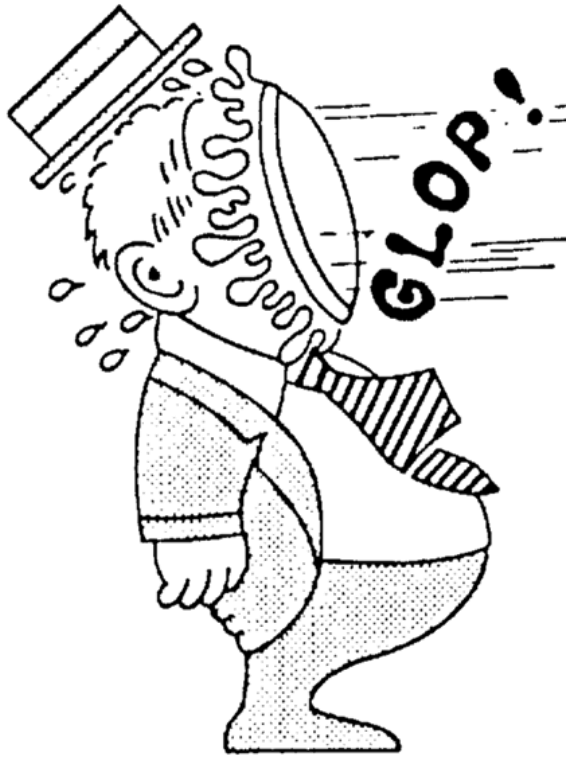
Absorção (Partição)

- Processo intrafacial e baseia-se na diferença de polaridade.



Mecanismo de separação

ABsorção



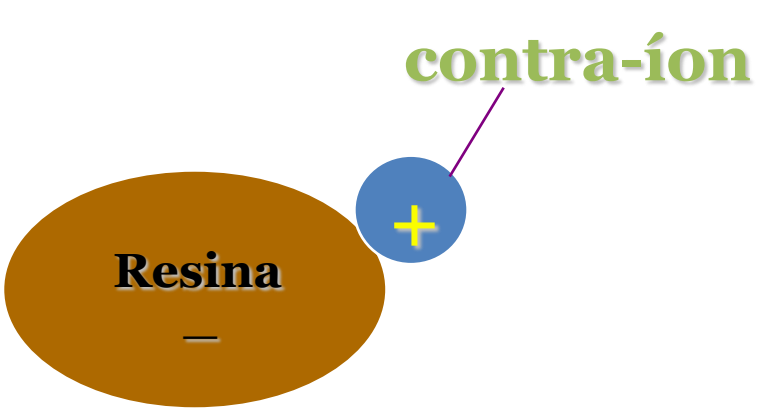
ADsorção

Diferença entre <u>Ab</u>sorção e <u>Ad</u>sorção

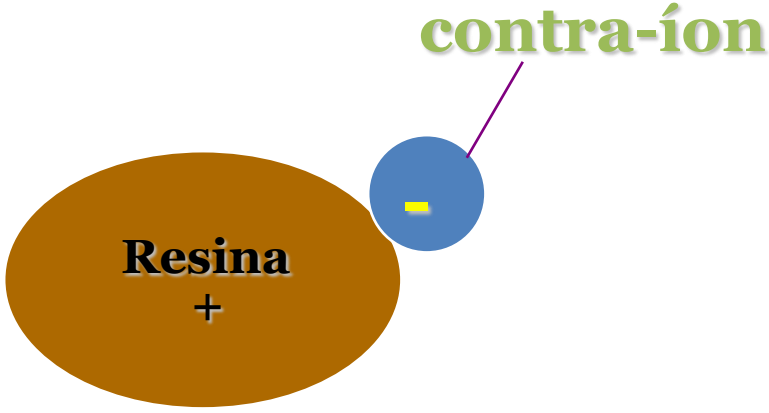
Mecanismo de separação

Troca iônica

- Processo químico onde na FE estão adicionados grupos ionizáveis.
- A FM é tamponante de acordo com o tipo de trocador usado.



Troca Catiônica

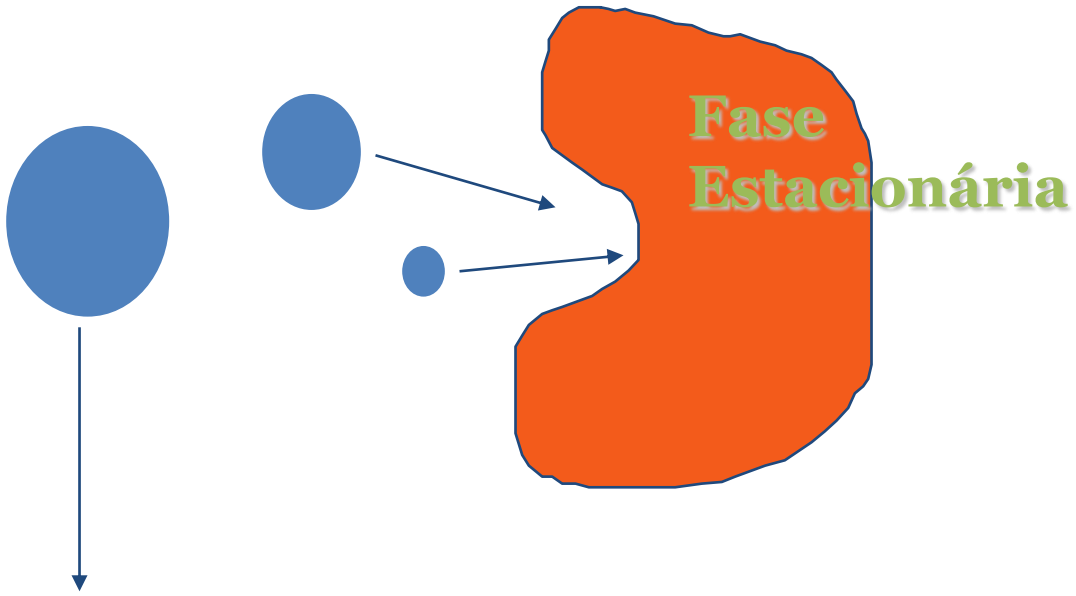


Troca Aniônica

Mecanismo de separação

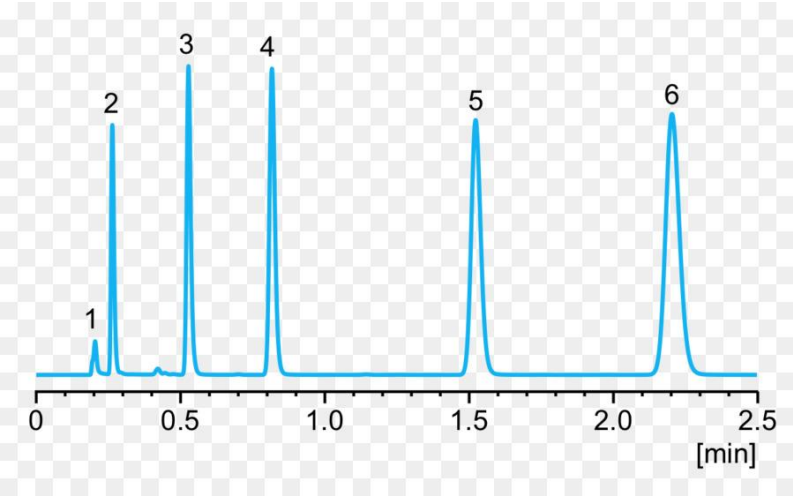
Exclusão

- Processo mecânico, onde partículas com tamanhos diferenciados são separadas.



Cromatografia liquida de alta eficiência (CLAE)

Cromatografia líquida de alta eficiência



Quais misturas podem ser separadas por CLAE ?

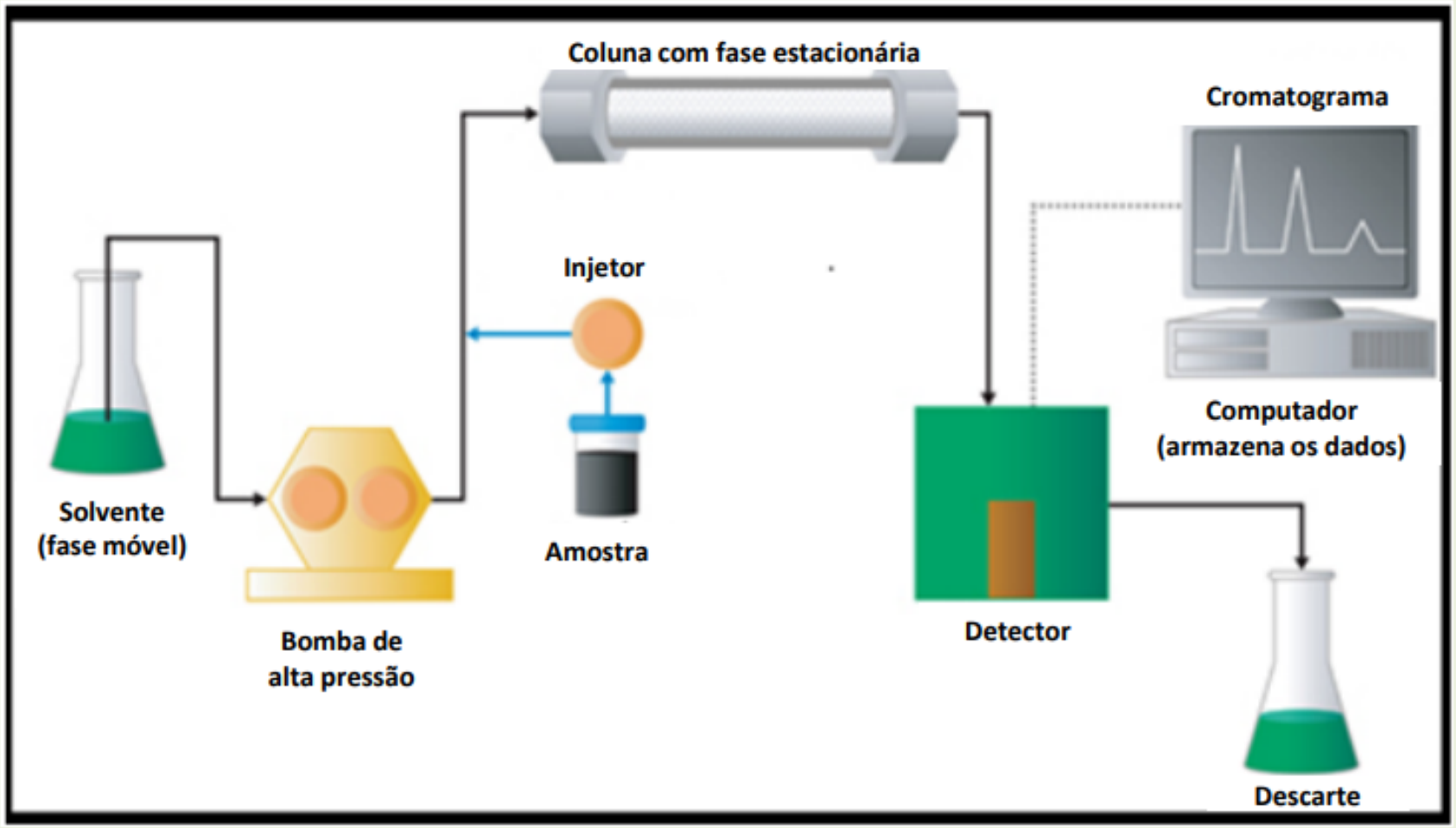
Para uma substância qualquer poder ser “arrastada” por um líquido ela deve dissolver-se nesse líquido.

Líquidos e sólidos

DE FORMA GERAL:

CL é aplicável para separação e análise de misturas cujos constituintes sejam solúveis na FM. Não há limitação de volatilidade ou de estabilidade térmica.

Cromatografia líquida de alta eficiência



Esquema de um cromatógrafo líquido

Cromatografia líquida de alta eficiência

FASE MÓVEL

- A fase móvel é o solvente que arrasta a amostra pela coluna (FASE ESTACIONÁRIA)
- A escolha da fase móvel depende:
  - Compostos a serem separados;
  - Tipo de coluna;

- Cuidados com os solventes:
  - Eliminação de impurezas;
  - Água ultrapura, solventes orgânicos;
  - Uso de filtros no reservatório da FM;

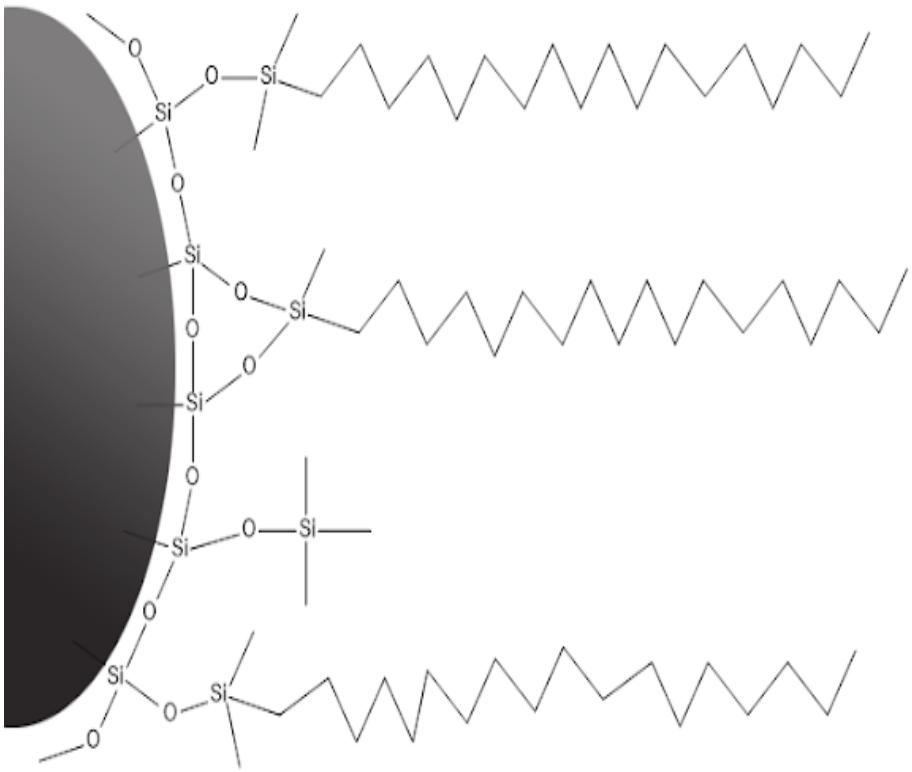
Cromatografia líquida de alta eficiência

Coluna (Fase estacionária)

- Material: aço inox
- Comprimento: 10 a 30 cm
- Diâmetro: 4 a 10 mm
- FE: Partículas de 5 a 10 mm
- Eficiência: 40 mil a 60 mil pratos/metro

Cromatografia líquida de alta eficiência

Coluna (Fase estacionária)



Coluna C18 (Octadecilsilano)

As fases estacionárias quimicamente ligadas são as fases mais importantes da cromatografia líquida.

Mais usado nos laboratórios de cromatografia.
Devido: estabilidade do ligante e por ser compatível com as análises em fase reversa (mais comuns utilizadas) e a maioria dos compostos orgânicos tem interações com essa coluna.

Cromatografia líquida de alta eficiência

Detectores

Dispositivos que examinam continuamente o material eluído, gerando sinal quando da passagem de substâncias.

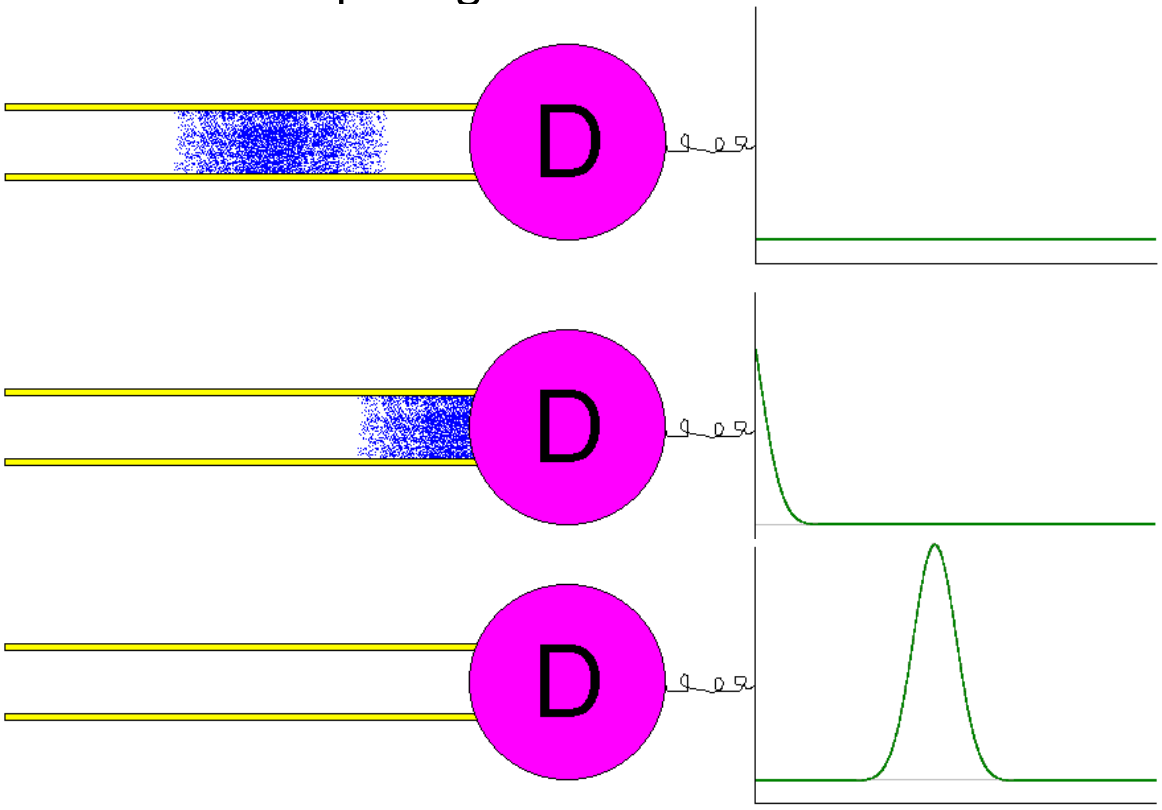
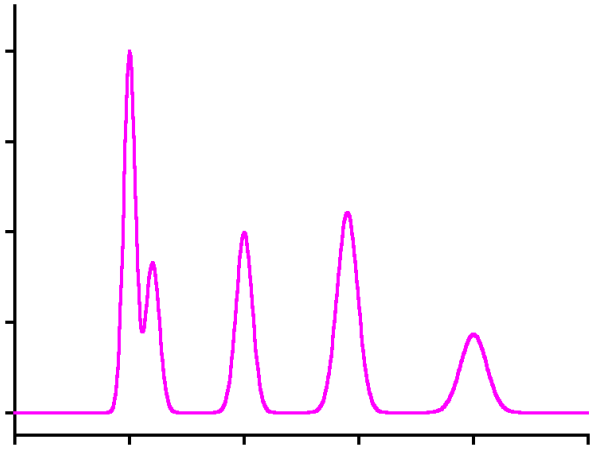


Gráfico Sinal x Tempo = ***CROMATOGRAMA***

Idealmente: cada substância separada aparece como um PICO no cromatograma.

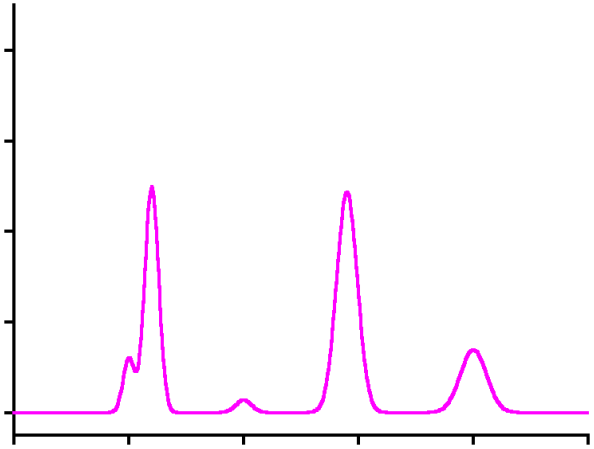
Cromatografia líquida de alta eficiência

Detectores



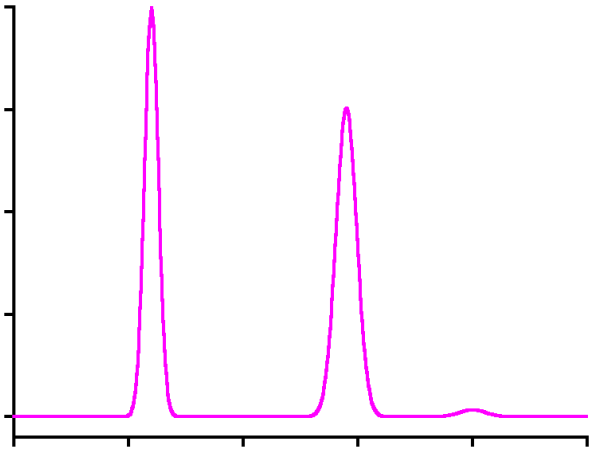
UNIVERSAIS:
Geram sinal para qualquer substância eluída.

Ex: ESPECTROMETRO DE MASSA



SELETIVOS:
Detectam apenas substâncias com determinada propriedade físico-química.

Ex: FLUORESCÊNCIA



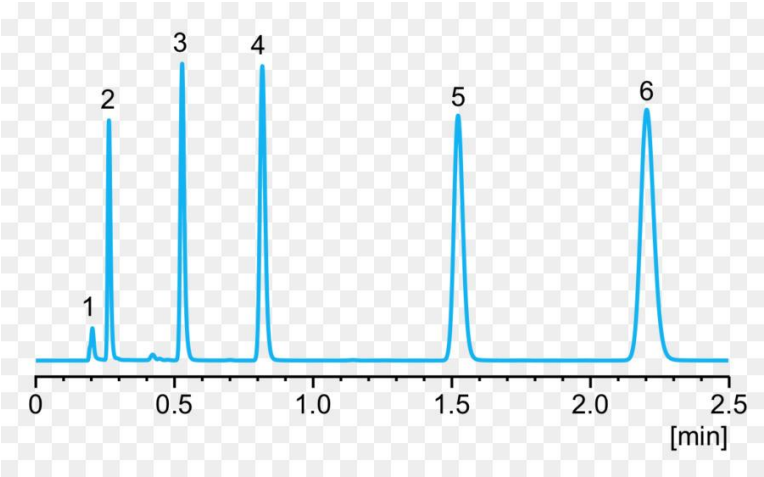
ESPECÍFICOS:
Detectam substâncias que possuam determinado elemento ou grupo funcional em suas estruturas

EX: DE NITROGÊNIO E FÓSFORO


DELL
HPLC tools

Cromatografia gasosa (CG)

Cromatografia gasosa



Quais misturas podem ser separadas por CG ?

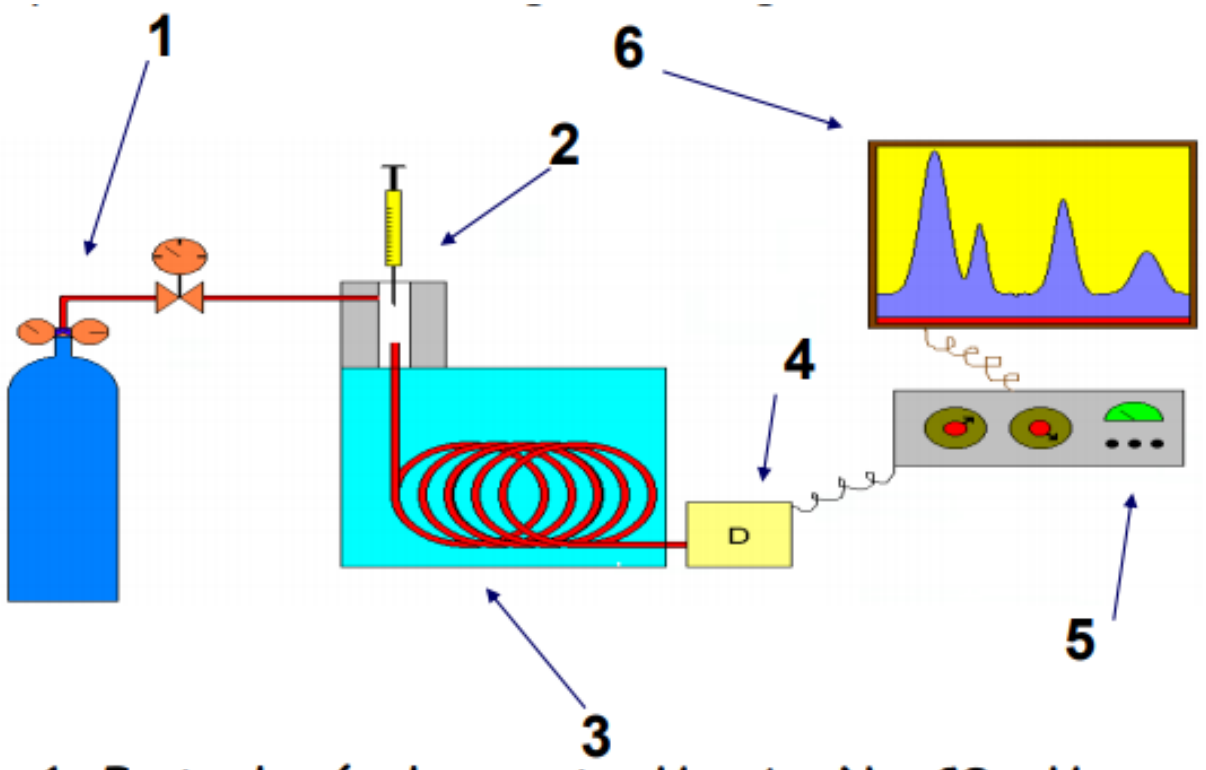
Para uma substância qualquer ser "arrastada" por um fluxo de um gás ela deve dissolver-se, pelo menos parcialmente, nesse gás.

Misturas cujos constituintes sejam
VOLÁTEIS (="evaporáveis")

DE FORMA GERAL:

CG é aplicável para separação e análise de misturas cujos constituintes tenham PONTOS DE EBULIÇÃO de até 300^{o}C e que sejam termicamente estáveis.

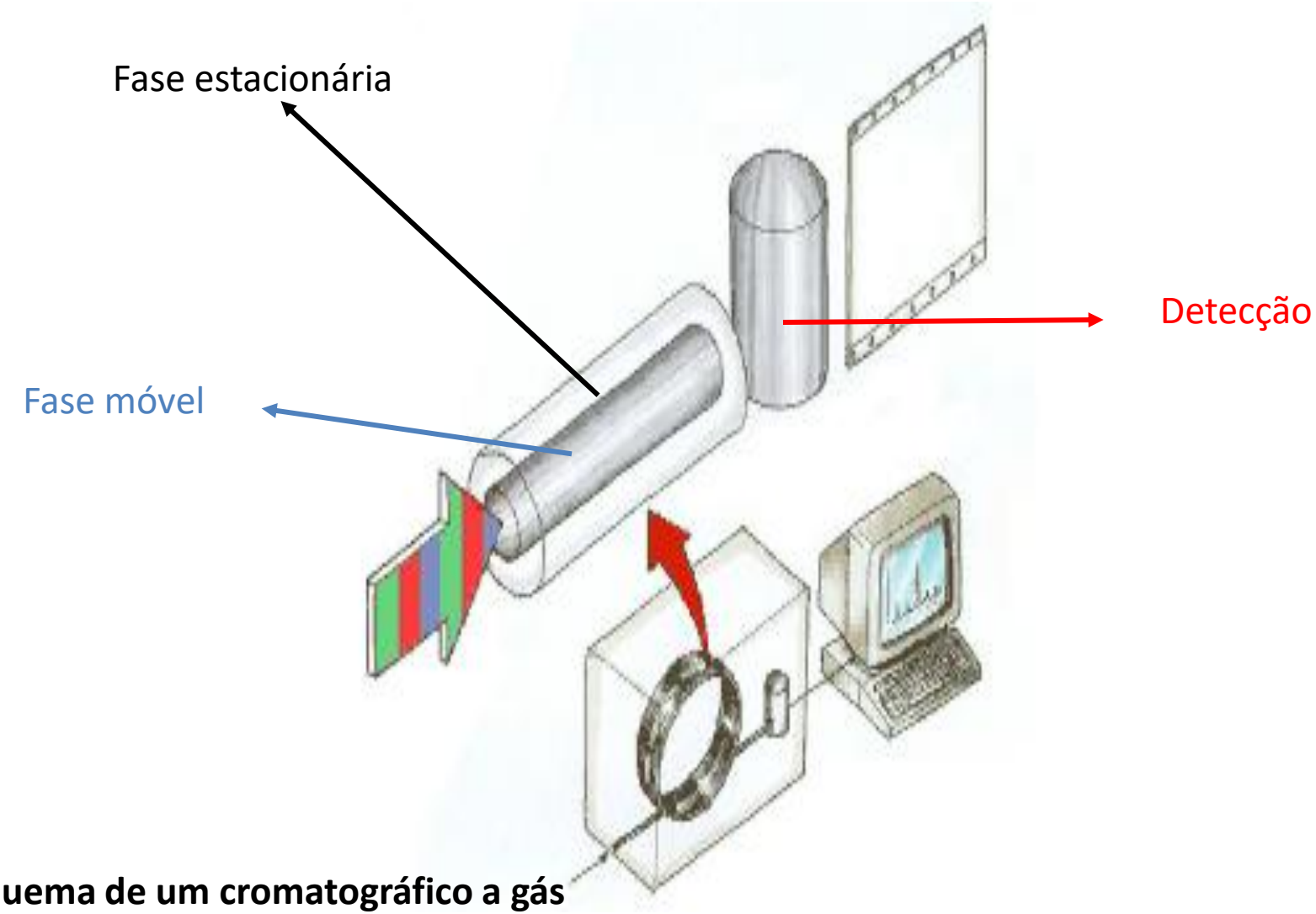
Cromatografia gasosa



- 1: Fonte do gás de arraste: He, Ar, N_2, CO_2, H_2
- 2: Sistema de injeção da amostra (poucos µL)
- 3: Coluna cromatográfica
- 4: Sistema de detecção
- 5: Amplificador de sinal
- 6: Registrador

Esquema de um cromatográfico a gás

Cromatografia gasosa



Esquema de um cromatográfico a gás

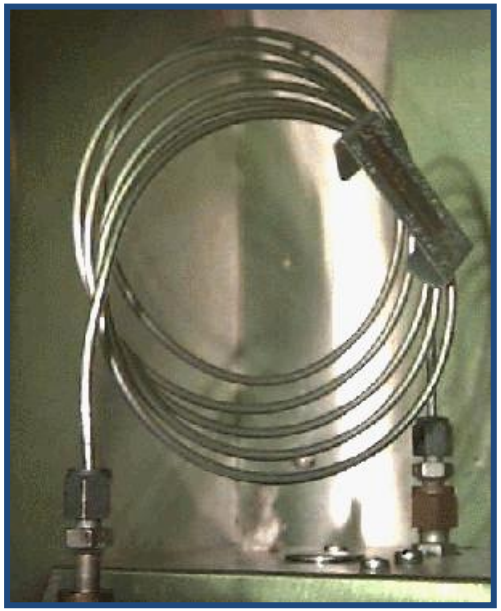
Fase Móvel - Gás de arraste

INERTE: Não deve reagir com a amostra, nem com a fase estacionária ou superfícies do instrumento.

PURO: Deve ser isento de impurezas que possam degradar a fase estacionária.

Mais usado HÉLIO

Fase estacionária - Colunas



EMPACOTADA

∅ = 3 a 6 mm

L = 0,5 m a 5 m

CAPILAR

∅ = 0,1 a 0,5 mm

L = 5 m a 100 m

Paredes internas recobertas com um filme fino (fração de μm) de FE líquida ou sólida

Cromatografia para análise de agrotóxico em arroz

Nas lavouras Brasil à fora, os agrotóxicos são utilizados para o controle de pragas, doenças e plantas daninhas.

O uso de agrotóxicos podem representar significativos riscos ambientais e à saúde humana quando produtores não utilizam produtos recomendados ou não seguem as especificações técnicas de aplicação.

Arroz recusado por exceder LMRs

Rice: FDA Rejected 95 Containers of Vietnam Rice Products for Pesticide Residue

Posted on October 5, 2016
By Michael Klein, USA Rice

Viet Nam, one of the largest producers and exporters of rice in the world, and one that comes under frequent suspicion of violating World Trade Organization (WTO) obligations, is under new scrutiny for violating U.S. food safety regulations.

Between January and August of this year, the U.S. Food and Drug Administration (FDA) rejected 95 shipping containers of jasmine rice and rice products from Viet Nam citing illegal pesticide residue in all

We were in the dark about Jordan's new residue norms, claims rice exporters body

Jordan's Agriculture Ministry has denied permission for offloading 12 containers carrying 270 tonnes of basmati rice from a North Indian exporter at its Aqaba port as Jordanian government laboratories found the pesticide residue in rice samples examined were higher than the maximum residue level (MRL).

"The samples were found to have residue level (of fungicide tricyclazole) higher than it is now permitted. However, what is strange was that Jordan did not notify its decision to revise MRL and as a result, this information was not publicly available," said AIREA Executive Director Rajen Sundaresan.

EU norms

"All of a sudden, Jordan has decided to adopt the European Union (EU) norms for tricyclazole residue, which stands at 0.01 parts per million (ppm). We had little knowledge about this," he said, adding that the association has already written to Apeda and Jordan Chamber of Commerce.

From January 1 this year, the EU decided to not allow the import of basmati rice whose tricyclazole levels exceed more than 0.01 ppm to its member countries, affecting most basmati exporters from India.

Prior to the implementation of new norms, the MRL in Indian basmati was 1 ppm. The tolerance levels for tricyclazole in the US and Japan, interestingly, are much higher, at 3 ppm and 10 ppm respectively.

Indian rice exporters have been lobbying with the Central government for getting the new norms relaxed by the EU for two years.

Distribuição de agrotóxicos no arroz

Tebuconazol - 150 g/hectare

1 aplicação em estágio R3

~18 mg ia/kg

13,6 mg ia/kg

SOLO + COLMO + FOLHAS

CASCA

3,3 mg ia/kg

1,1 mg ia/kg

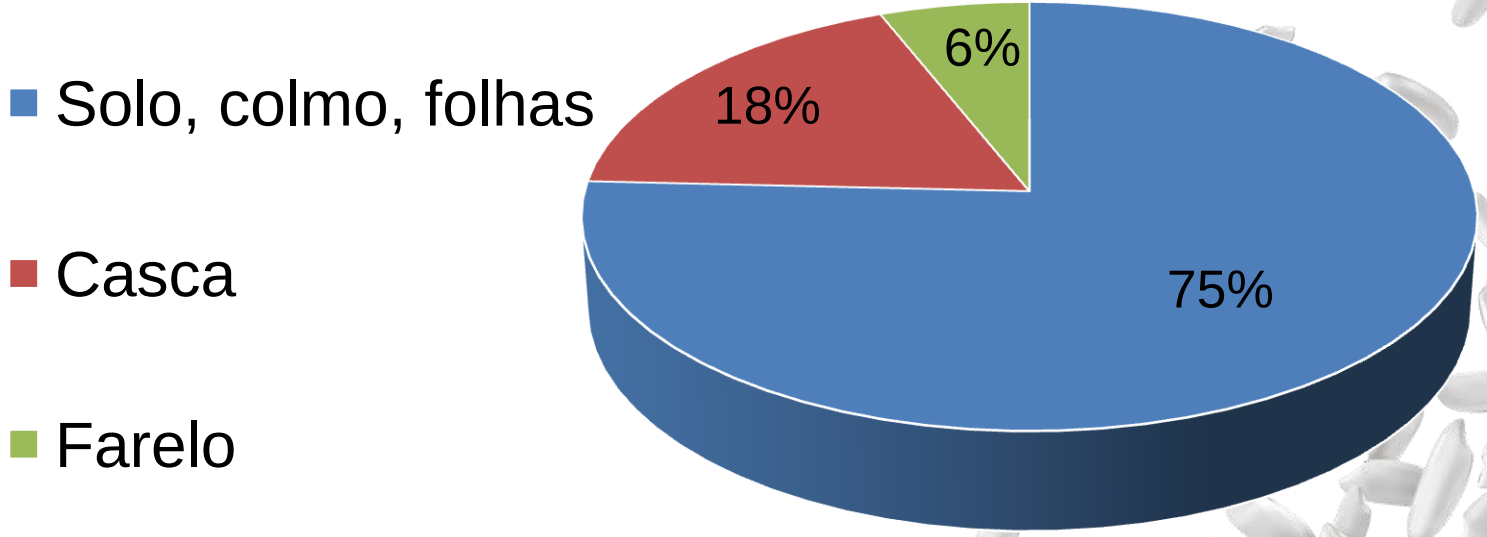
FARELO

Fonte: Dors et al., J. Braz. Chem. Society, 22 (10), 1921-1930, 2011.

Distribuição de agrotóxicos no arroz

Arroz polido <0,01 ppm

Arroz integral ~0,13 ppm



Fonte: Dors et al., J. Braz. Chem. Society, 22 (10), 1921-1930, 2011.

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Analytical Methods

Development and validation of a multianalyte method for quantification of mycotoxins and pesticides in rice using a simple dilute and shoot procedure and UHPLC-MS/MS

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ARTICLE INFO

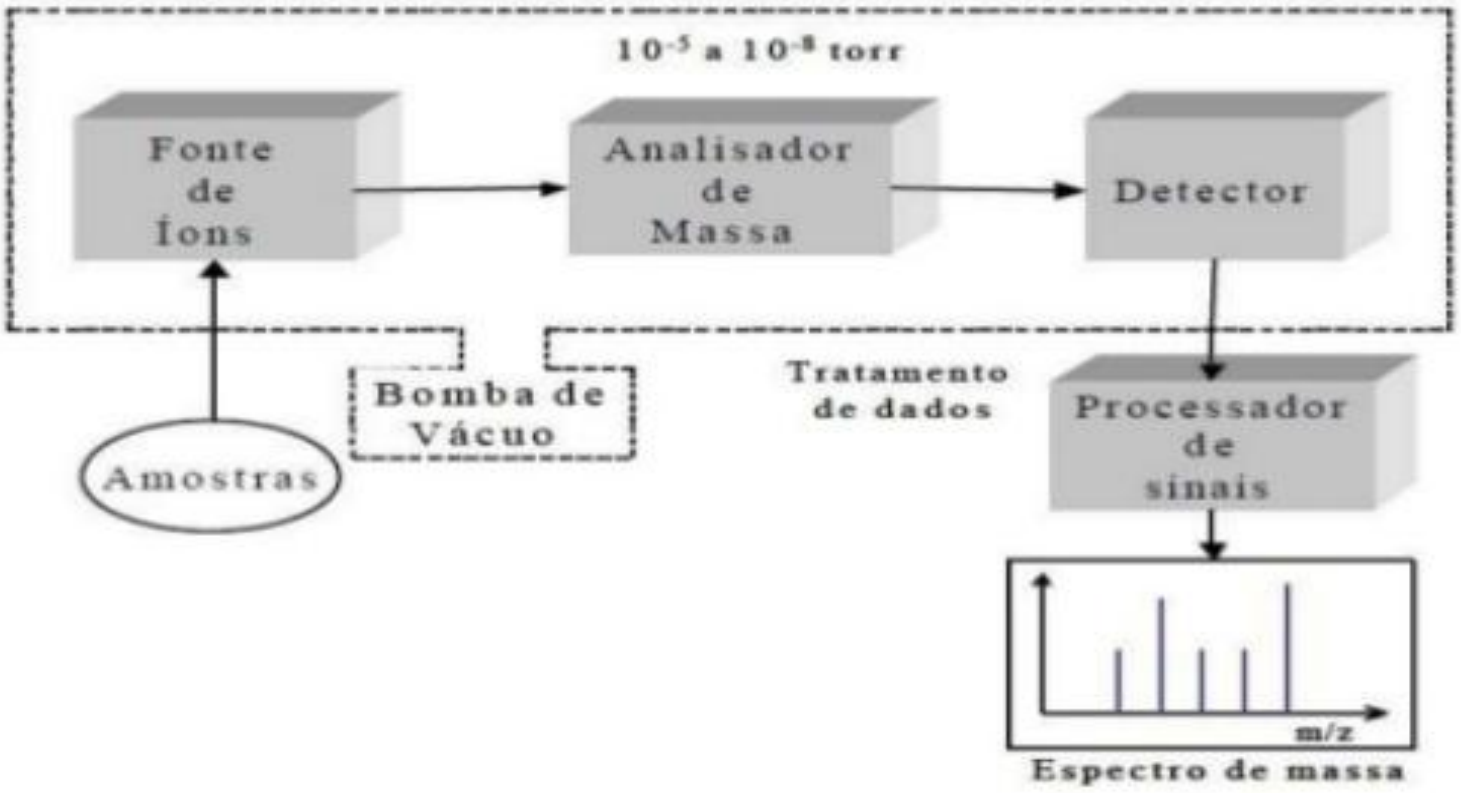
Keywords:
Dilute and shoot
Ultra-high performance liquid chromatography
Tandem mass spectrometry
Mycotoxins
Pesticides

ABSTRACT

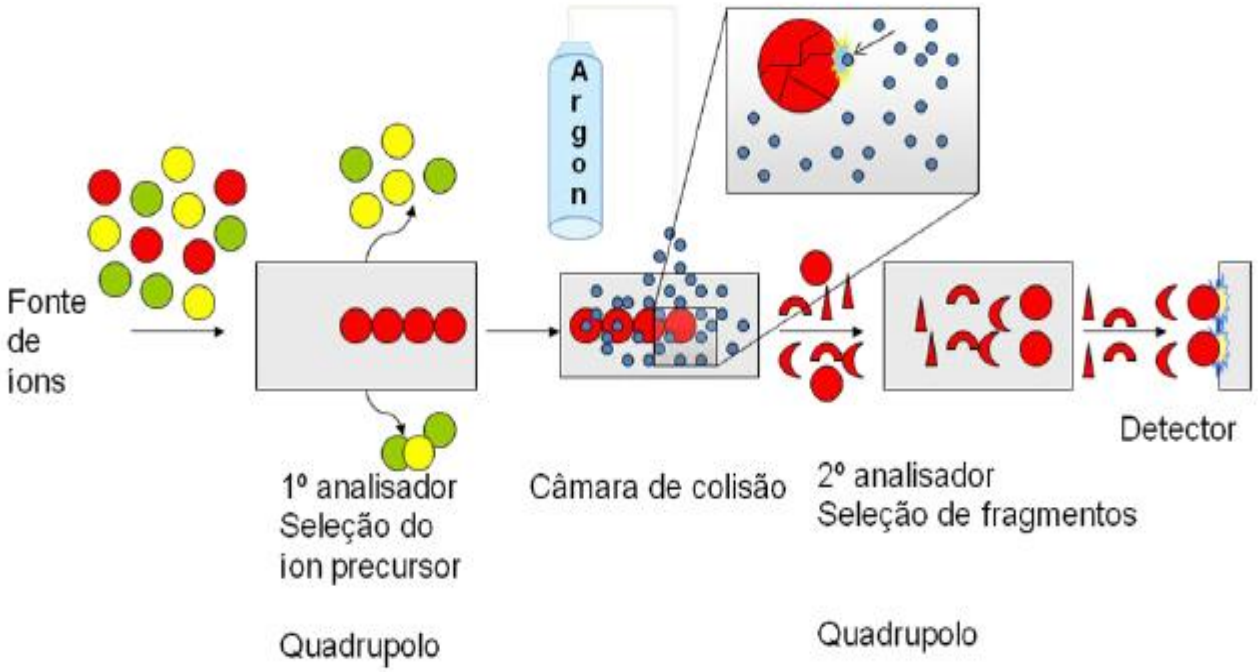
In the present manuscript an analytical methodology for the simultaneous determination of ten mycotoxins and six pesticides in rice was developed. This methodology comprises the application of the dilute and shoot protocol followed by quantification via UHPLC-MS/MS. The methodology was validated and all figures of merit shown to be within the limits established by regulation. Hence, the recoveries for mycotoxins and pesticides were within the specified ranges. Precision was assessed by repeatability and intra-laboratory reproducibility with standard deviations smaller than or equal to 20%. The limits of detection, quantification and decision as well as the detection capacity were determined by the analytical curves whereas the measurement uncertainty was established by applying the bottom-up approach. Finally, the current methodology was applied to samples of rice (n = 42) commercialized in Brazil and positive results were found in only two for deoxynivalenol and zearalenone.

DETECTOR
Espectrômetro de massas

Componentes básicos



DETECTOR
Espectrômetro de massas



Esquema de um equipamento do tipo Triplo Quadrupolo, onde os dois Analisadores estão separados por uma Câmara de Colisão.

Análise “multiresíduo”

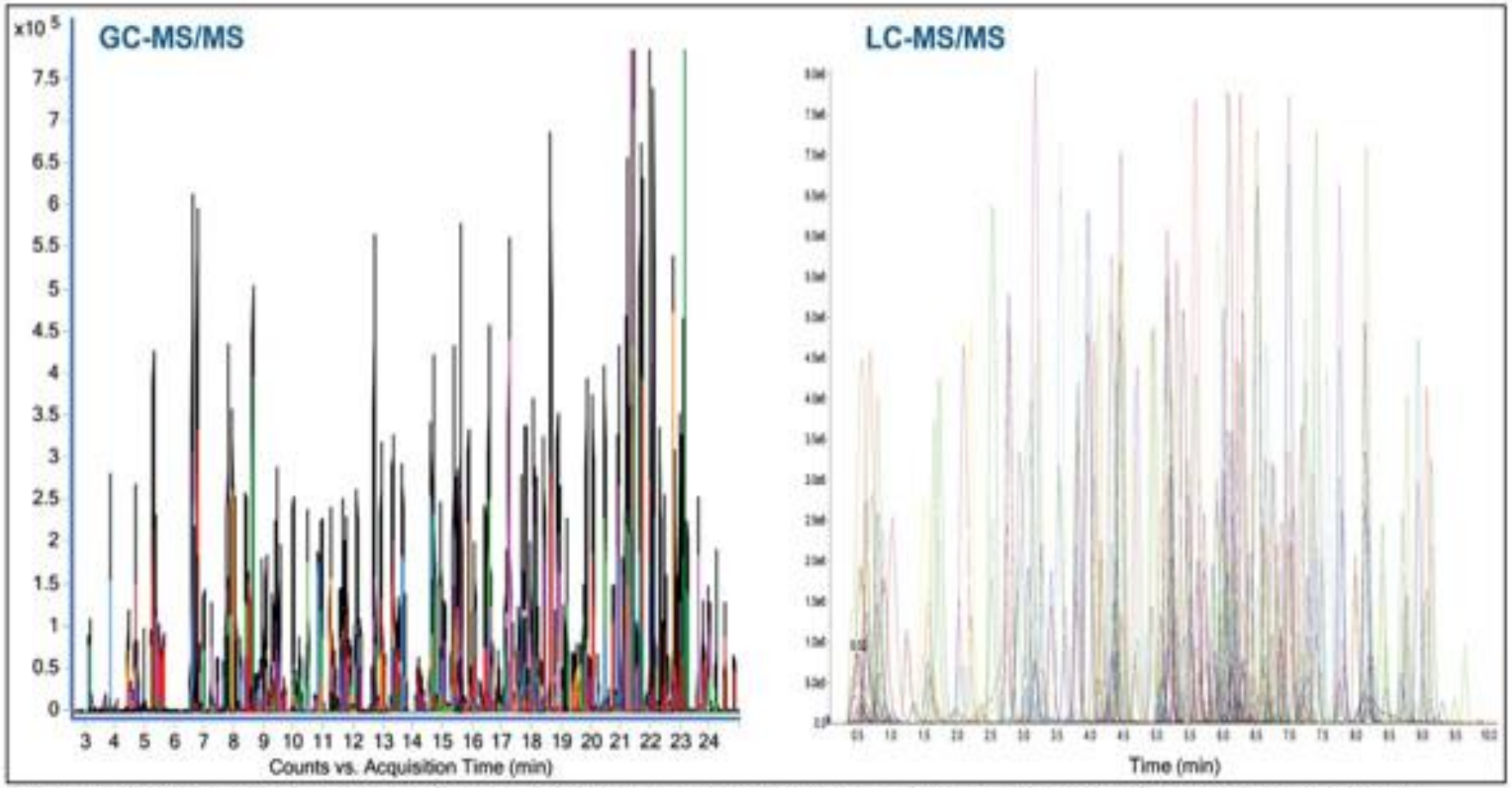
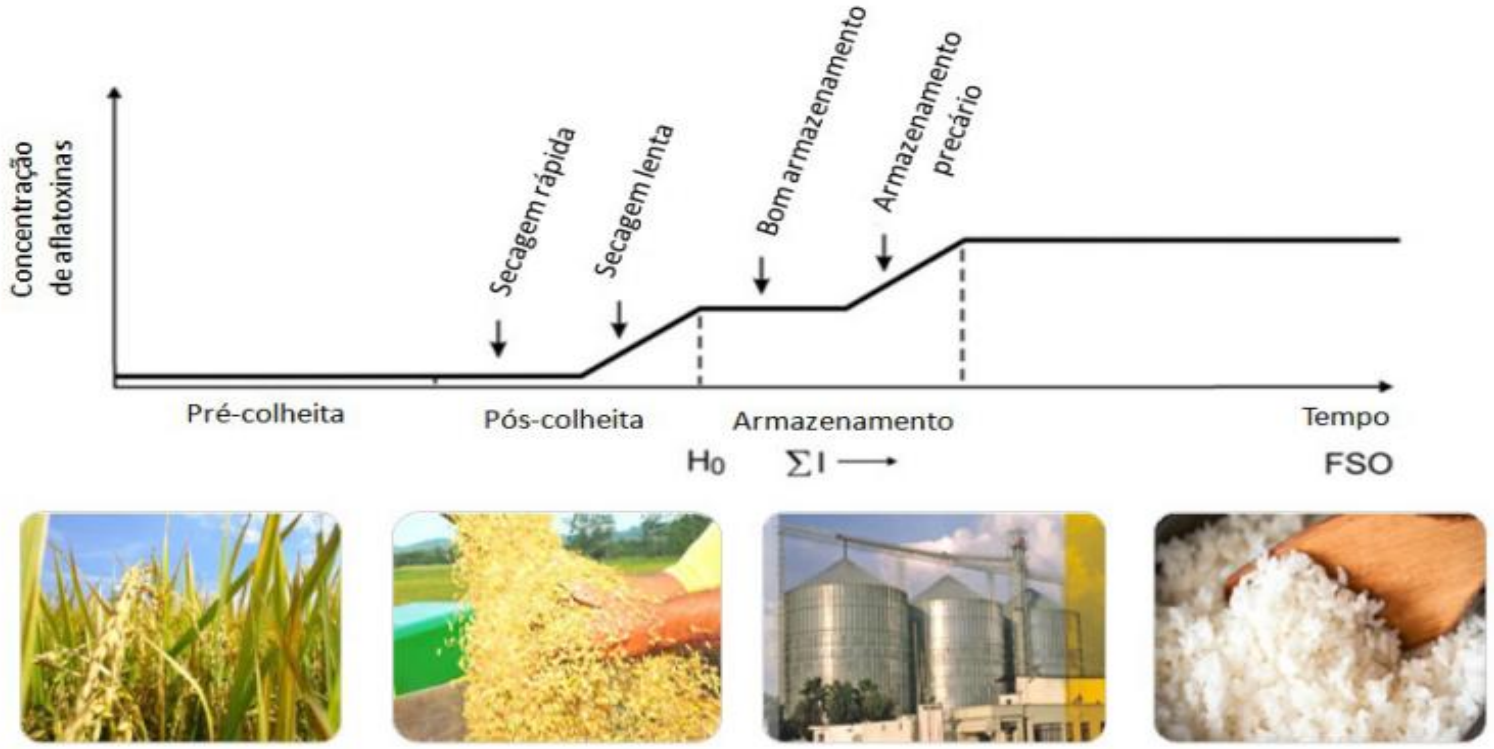


Figure 1: Chromatograms Obtained in Multiresidue Analyses of More than 300 Pesticides Analyzed by GC-MS/MS and LC-MS/MS

Cromatografia para análise de micotoxinas em arroz

Micotoxinas metabólitos secundários produzidos por fungos.

Já encontradas no arroz, destacam-se: aflatoxinas (AFs), Ocratoxina A (OTA), Desoxinivalenol (DON), Zearalenona (ZON) e Fumonisina (FUM).



Formação de aflatoxinas durante a cadeia produtiva de pequenos grãos (PITT et al., 2013).

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Occurrence and simultaneous determination of nivalenol and deoxynivalenol in rice and bran by HPLC-UV detection and immunoaffinity cleanup

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Brown rice
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Nivalenol
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White rice

ABSTRACT

A simple and accurate method for simultaneously quantifying two co-occurring *Fusarium* mycotoxins in rice and bran, nivalenol (NIV) and deoxynivalenol (DON), is described. The method involves the use of an immunoaffinity column for cleanup and HPLC-UV detection for quantification. The limits of quantification were <11.09 μg kg^{-1} for the two toxins in rice and bran. The mean recoveries from blank samples spiked at levels of 100–1000 μg kg^{-1} were 86.2–106.6% for NIV and 93.1–106.2% for DON, with relative standard deviations of 6–15% for NIV and 3–11% for DON, respectively. The detection rate of NIV in 482 rice and 239 bran samples was 34–96%, where the level ranging from 5.7 to 2791.4 μg kg^{-1}, whereas that for DON was 10.4–44.8% with levels ranging from 7.1 to 655.6 μg kg^{-1}. The co-occurrence rates of NIV and DON were 9.1%, 14.9%, and 41.5% for white rice, brown rice, and bran, respectively. The estimated dietary intakes of NIV and DON for the Korean population based on the occurrence data were well below

Deoxinivalenol e Nivalenol

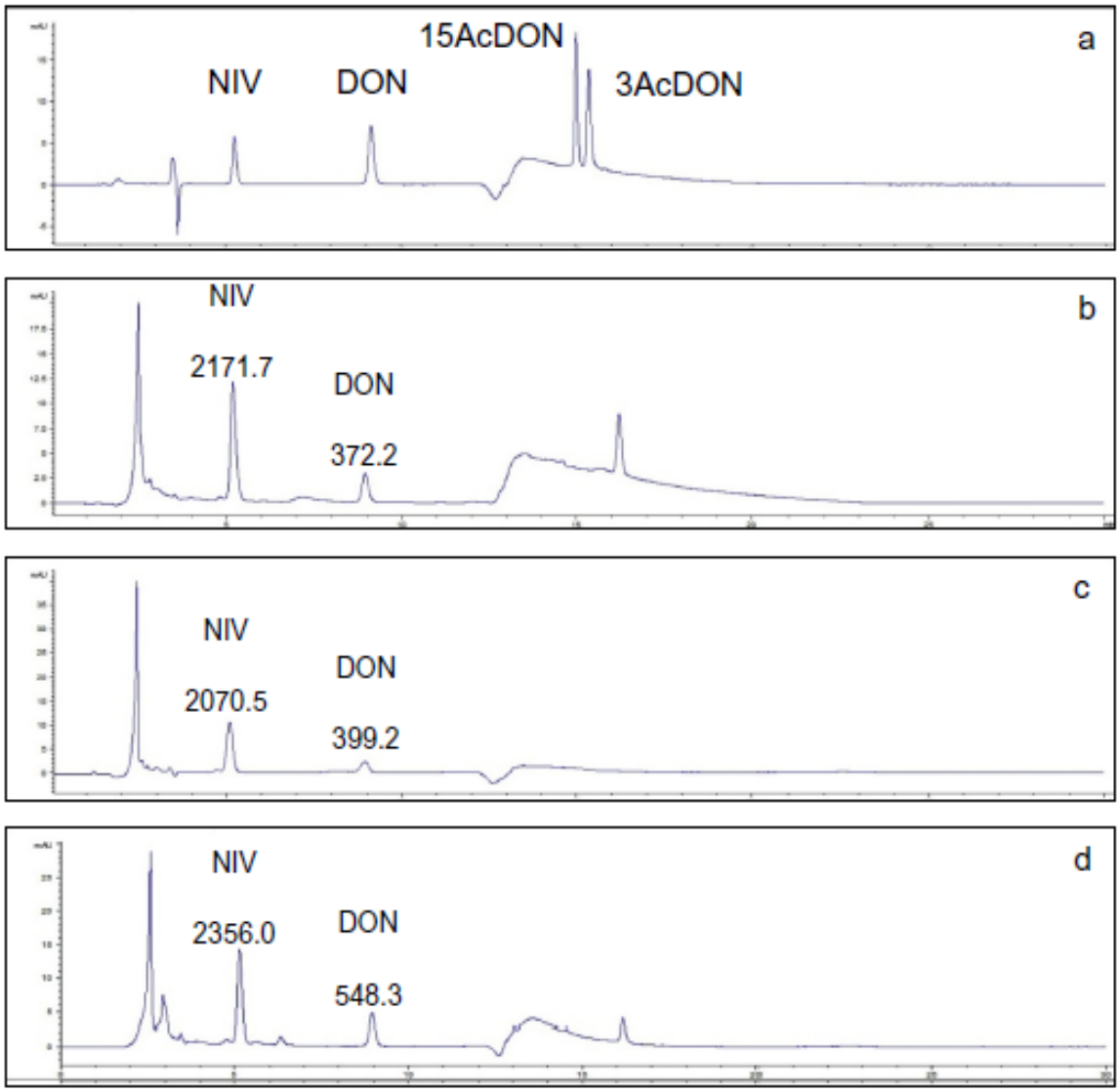

Fig. 1. HPLC–UV chromatograms obtained for nivalenol (NIV) and deoxynivalenol (DON) in standard solution (a)[a] and naturally contaminated white rice (b), brown rice (c), and bran (d). [a]A standard solution comprising NIV (500 ng mL^{-1}), DON (500 ng mL^{-1}), 3-acetyl-deoxynivalenol (3-ADON) (500 ng mL^{-1}), and 15-ADON (500 ng mL^{-1}) was used to obtain this chromatogram.

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Determination of multiple mycotoxins in feedstuffs by combined use of UPLC–MS/MS and UPLC–QTOF–MS

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Feedstuffs
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Mass spectrometry
UPLC–MS/MS
UPLC – QTOF – MS

ABSTRACT

In this report, a UPLC–ESI–MS/MS method for the simultaneous determination of aflatoxins, ochratoxin A, zearalenone, deoxynivalenol, fumonisins, T-2 and HT-2 toxins, fusarenone X, diacetoxyscirpenol, and 3- and 15-acetyldeoxynivalenol in feedstuffs was developed. A quadrupole-time-of-flight mass spectrometer detector (QTOF–MS) operating in full scan mode was combined with the UPLC–ESI–MS/MS system to confirm the identity of detected mycotoxins and to identify other possible microbial metabolites occurring in samples. Sixty-two feed samples from the Spanish market were analyzed. Extraction of metabolites was carried out with acetonitrile-water-formic acid (80:19:1, v/v/v). Method detection and quantification limits and performance criteria set by Commission Regulation (EC) No 401/2006 were fulfilled. Relatively high levels of the main regulated mycotoxins and presence of non-regulated mycotoxins in feed samples were found. This is the first study in which mycotoxins and other microbial metabolites occurring in feed are studied using a UPLC–QTOF–MS system being therefore a reference report.

Cromatografia para análise de compostos fenólicos

✓Determinação de compostos fenólicos em arroz

✓Os metabólitos primários e secundários têm sido usados para discriminar a origem geográfica dos alimentos.

✓ cromatografia gasosa e a cromatografia líquida, acopladas à espectrometria de massa tem sido utilizada.

✓Análise de fenólicos

Cromatografia para análise de compostos fenólicos

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Food Chemistry

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Cooking quality properties and free and bound phenolics content of brown, black, and red rice grains stored at different temperatures for six months

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ARTICLE INFO

Keywords:
Oryza sativa
Postharvest quality
Flavonoids
Phenolic acids

ABSTRACT

The changes in cooking quality and phenolic composition of whole black and red rice grains stored during six months at different temperatures were evaluated. Brown rice with known cooking quality properties and low phenolic levels was used for purposes comparison. All rice genotypes were stored at 13% moisture content at temperatures of 16, 24, 32, and 40 °C. Cooking time, hardness, free and bound phenolics, anthocyanins, proanthocyanidins, and free radical scavenging capacity were analysed. The traditional rice with brown pericarp exhibited an increase in cooking time and free phenolics content, while rice with black pericarp exhibited a reduction in cooking time after six months of storage at the highest studied temperature of 40 °C. There as increases in ferulic acid levels occurred as a function of storage temperature. Red pericarp rice grains showed decreased antioxidant capacity against ABTS radical for the soluble phenolic fraction with increased time and storage temperature.

Cromatografia para análise de compostos fenólicos

Table 4
Bound phenolic content (μg g^{-1}) of brown, black, and red pericarp rice grains stored at different temperatures for six months.

Storage temperature (°C)	*p*-Coumaric	Ferulic	Quercetin
Brown			
Initial	51.5 ± 0.4 e*	225.1 ± 0.5 b	nd**
16	53.1 ± 0.0 de	237.8 ± 0.0 a	nd
24	52.7 ± 0.2 e	220.5 ± 0.3 bc	nd
32	54.4 ± 0.9 d	226.2 ± 2.1 b	nd
40	46.2 ± 0.3 f	212.3 ± 1.1 cd	nd
Black			
Initial	35.2 ± 0.5 h	179.7 ± 4.3 f	1.6 ± 0.0 a
16	39.0 ± 0.2 g	207.2 ± 4.6 d	1.2 ± 0.0 b
24	35.6 ± 0.1 h	181.7 ± 3.8 ef	0.9 ± 0.0 c
32	35.5 ± 0.2 h	182.9 ± 0.9 ef	1.1 ± 0.0 b
40	34.6 ± 0.4 h	179.6 ± 0.1 f	1.6 ± 0.0 a
Red			
Initial	65.4 ± 0.4 a	217.5 ± 2.5 bc	nd
16	63.2 ± 0.2 b	206.9 ± 0.3 d	nd
24	66.2 ± 0.3 a	204.9 ± 1.8 d	nd
32	61.8 ± 0.4 b	207.8 ± 1.2 d	nd
40	56.3 ± 0.7 c	188.6 ± 0.3 e	nd

* Simple arithmetic means of three replicates ± standard deviation. Different lower case letters within a column indicate significant difference by Tukey's test ($p \leq 0.05$).
** nd = not detected.

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Research Article

Discrimination of genotype and geographical origin of black rice grown in Brazil by LC-MS analysis of phenolics

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ARTICLE INFO

Keywords:
Oryza sativa
Rice authenticity
Brazilian rice
Flavonoids
Anthocyanins

ABSTRACT

Physicochemical properties, cooking time, and phenolics profile of two black rice genotypes grown at six different locations in Brazil were determined. The cultivar IAC 600 and the elite-line AE 153045 were used. The main growing locations for black rice were considered, as follows: Alegrete (ALG), Capão do Leão (CPL), Guaratinguetá (GUA), Roseira (ROS), Santa Vitória do Palmar (SVP), and Taubaté (TBT). Principal component analysis (PCA) and supervised partial least squares-discriminant analysis (PLS-DA) from liquid chromatography-mass spectrometry (LC-MS) data sets showed distinction among genotypes and locations. Quercetin-3-*O*-glucoside and vanillic acid were the most relevant compounds for discriminating genotypes. SVP location provided the most distinctive black rice, with greater total phenolics content. Characteristics of black rice from SVP location were associated to effects of latitude and wind conditions. Hesperetin, vanillic acid, quercetin-3-O-glucoside, and *p*-coumaric acid were the most relevant compounds for discriminating locations.

Exemplo de cromatograma –

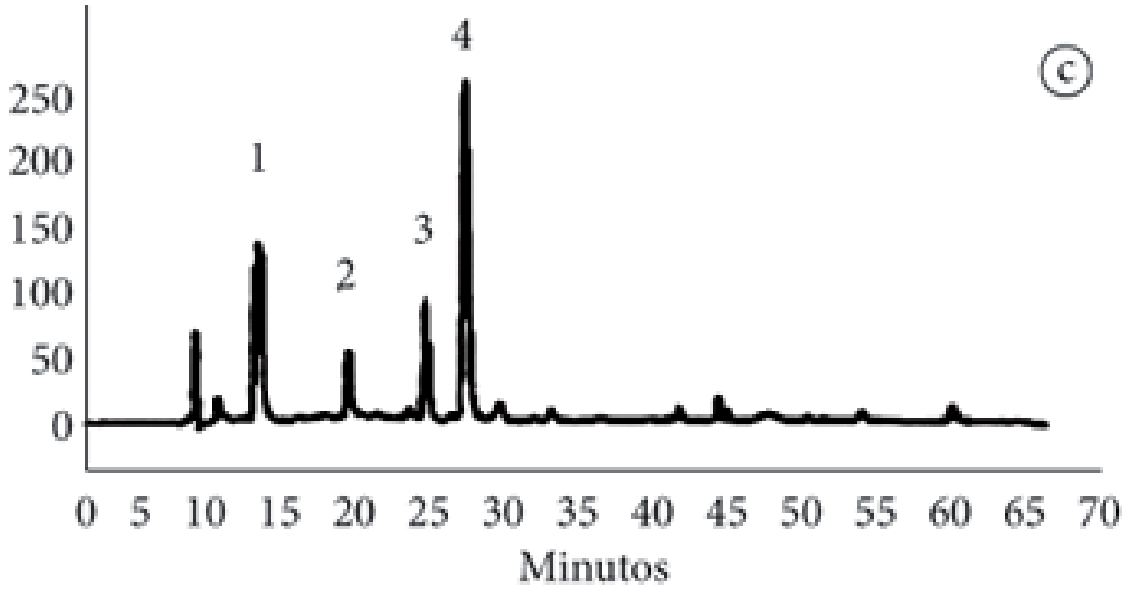

Figura 5. Cromatogramas das frações solúvel e insolúvel de uma amostra de arroz-preto: a) fração solúvel antes da hidrólise; b) depois da hidrólise; e c) fração insolúvel.

Mira et al., 2008. Ciênc. Tecnol. Aliment. vol.28 no.4 Campinas Oct./Dec. 2008

Cromatografia para análise de proteínas

- ✓Distribuição molecular de proteínas de arroz

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Improvement of the quality of parboiled rice by using anti-browning agents during parboiling process

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Glycine-treated rice
Reduced glutathione
Rice whiteness

ABSTRACT

Browning occurs in parboiled rice as a result of the Maillard reaction that negatively affects consumers' acceptability. The aim of this study was to evaluate the ability of gallic acid, glycine, reduced glutathione and L-cysteine at 0.1, 0.5, 1.0 and 2.0% levels to inhibit browning reactions during the parboiling of rice. Gallic acid and L-cysteine did not exhibit browning inhibition effect at the studied levels. On the other hand, glycine and the higher concentrations of reduced glutathione (1.0 and 2.0%) were able to promote a whiter color and a low free 5-hydroxymethyl-2-furaldehyde content (HMF). The highest level of 2.0% for glycine and reduced glutathione favored protein extractability and a weaker protein-starch matrix, roughly increasing the broken grains percentage. Cooking time changed just for reduced glutathione-treated rice, as a result of their weaker protein-starch matrix and the greater ability of the grains to soften during cooking.

Cromatografia para análise de proteínas

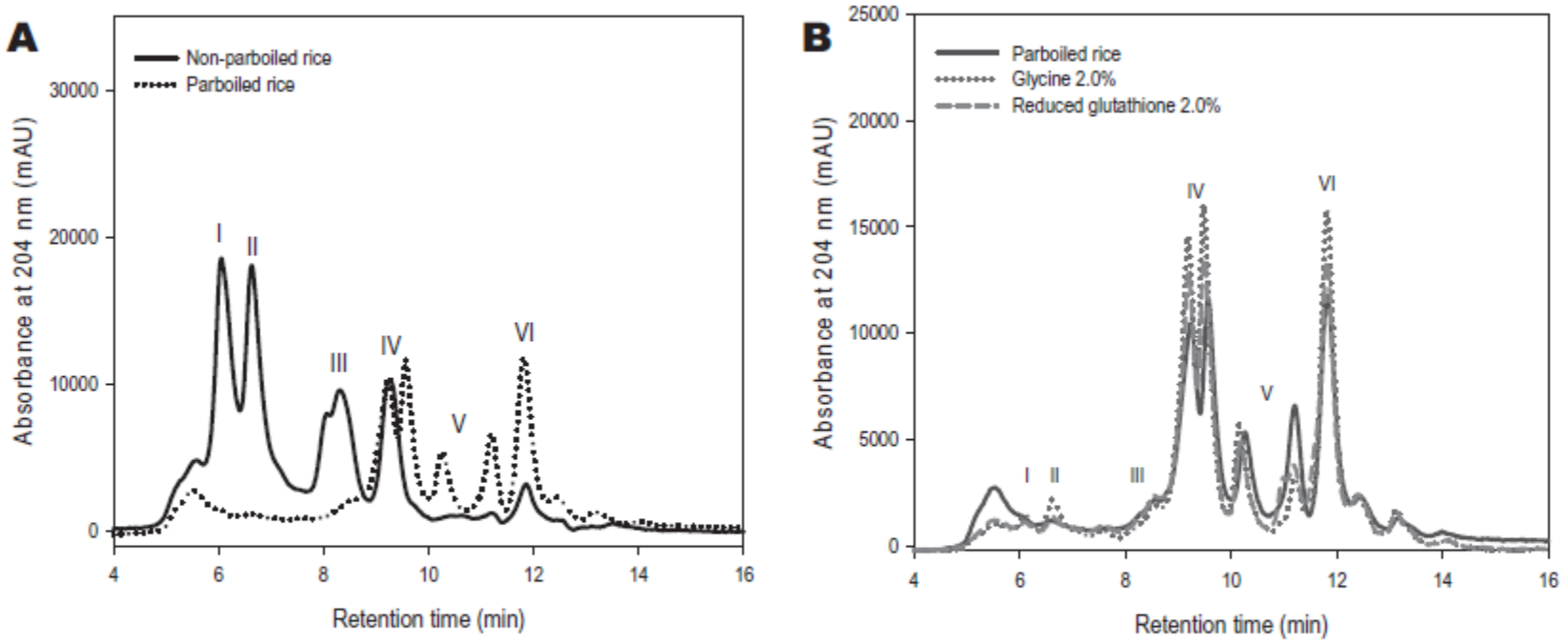

Fig. 3. Molecular weight distribution profiles of proteins in non-parboiled and parboiled rice (A), and comparative protein extractability profile between control treatment and glycine- and reduced glutathione-treated rice at the highest level of 2.0% (B). Fractions I and II indicate the region comprised by dimers, trimers and more polymerized forms of proteins; fraction III indicate the chromatogram region comprised by (α-β) glutelin subunit pairs; fraction IV indicate the region comprised by α- and β-glutelin subunits of rice glutelins; and fractions V and VI indicate the low molecular weight albumins, globulins and/or prolamins.

Cromatografia para análise de compostos voláteis

Volatile compounds profile of Brazilian aromatic brown rice genotypes and its cooking quality characteristics

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Abstract

Background and objectives: This study evaluated the volatile profile by solid-phase microextraction (SPME)-gas chromatography/mass spectrometry (GC/MS) and the cooking quality properties of seven aromatic and one non-aromatic rice genotypes grown in Brazil.

Findings: Twenty-three volatile compounds were identified by SPME-GC/MS analysis. PCA and PLS-DA allowed the separation of aromatic and non-aromatic genotypes. PLS-DA analysis revealed six compounds as discriminating between groups: 2-acetyl-1-pyrroline (2-AP), decanal, 2-hexanone, 2-pentylfuran, 1-hexanol, and hexanal. 2-AP was detected only in aromatic genotypes, and the content varied from 0.21 to 0.57 μg/g. Cooking time changed from 23.5 to 38.3 min in the new aromatic genotypes while hardness changed from 52.7 to 100.7 N.

Conclusions: Our study revealed six volatile compounds as discriminants between aromatic and non-aromatic genotypes grown in Brazil. 2-AP was identified only in aromatic genotypes. Genotype BR5 exhibited the best general performance since their volatile compounds results indicate less off-flavors (hexanal), higher 2-AP content, and similar cooking time and hardness to IRG and JAS.

Significance and novelty: Results may help rice chain in selecting Brazilian genotypes of aromatic rice to be grown in Brazil and distributed worldwide. Also, this work may serve as a starting point for future work on aromatic rice authenticity.

Cromatografia para análise de arsênio

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journal homepage: www.journals.elsevier.com/food-chemistry-x

Arsenic speciation analysis in rice milk using LC-ICP-MS

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ARTICLE INFO

Keywords:
Arsenic speciation
LC-ICP-MS
Rice milk

ABSTRACT

The consumption of rice milk has increased, mainly by individuals intolerant to lactose or allergic to cow milk. However, rice milk contains As. In this sense, the concentration of As in rice milk should be controlled. In the present study it is proposed a methodology for determination of As(III), dimethylarsenic (DMA), monomethylarsenic (MMA) and As(V) species in rice milk using LC-ICP-MS. The main features of the methodology are fast analysis, easy and simple sample preparation, where the sample is 3-fold diluted in the mobile phase and then filtered. The four arsenic species investigated were detected in the analysed samples, being As(V) the main species. The limit of quantification of the method ranges from 0.25 to 0.43 $\mu g\ L^{-1}$ As. The analyte recovery ranged from 81 to 116% for samples spiked to 1.00 $\mu g\ L^{-1}$ or 5.00 $\mu g\ L^{-1}$ As and the relative standard deviation was better than 5%.