Inverse Gas Chromatographic Measurement of Flavor Interactions with Solid Food Matrices under Controlled Relative Humidity

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Project Objectives

1. Evaluate by IGC the binding properties of selected volatile probes (aldehydes, esters, ketones, alcohols and hydrocarbons) on commercial soy protein isolate (SPI).

2. Modify IGC system and develop method for investigation of interaction/competition between selected volatile probes (binary mixtures) and SPI.

3. Interface IGC with APCI-MS detector and evaluate system for the simultaneous testing of multiple volatile probes and their binding interactions.

4. Apply IGC to measure and compare aroma binding/retention properties of a soda cracker model, formulated with and without added SPI, using selected key butter aroma compounds as volatile test probes.

Background and Motivation

- Flavor (volatile) – matrix (ingredient) interactions may impact flavor quality
  - flavor release
  - imbalanced flavor

- Soy (protein) food products
  - increased popularly due to potential health benefits
  - flavor acceptability issues
    - off-flavors
    - flavor binding (flavor fade)

- Flavor-soy protein binding poorly understood
  - methods needed for evaluation (low moisture foods)
  - methods that can relate to sensory response

Measurement of flavor-food matrix interactions . . . .

- **liquid systems**[1]**:**
  - equilibrium dialysis (liquid-liquid equilibrium)
  - static headspace (vapor-liquid equilibrium)

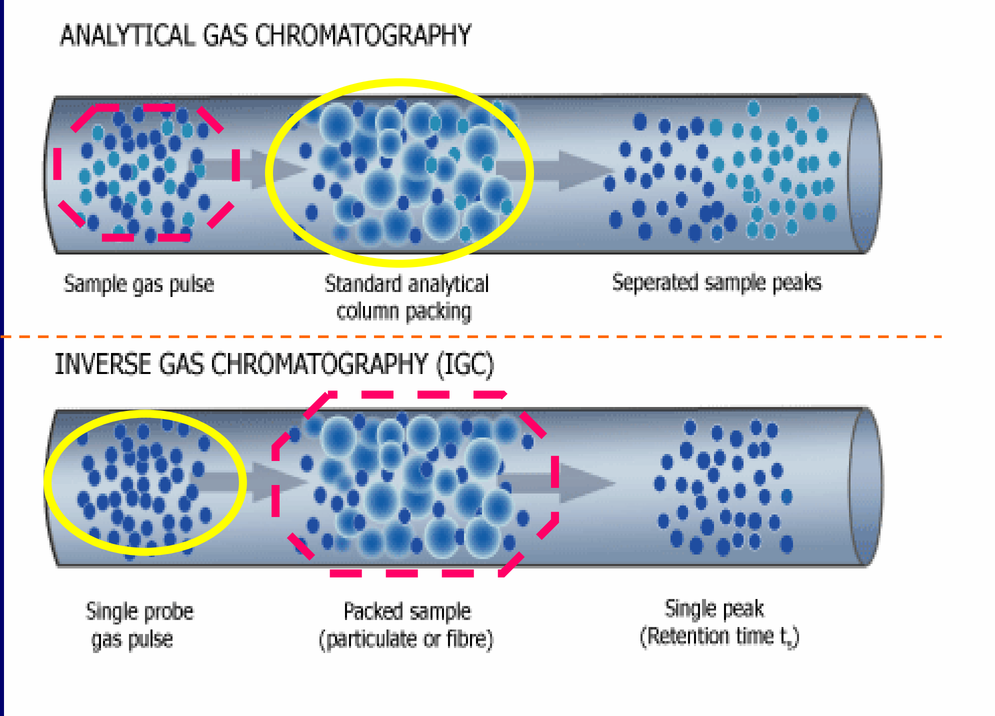
    *limitations: not sensitive, slow, unsuitable for solid foods

- **solid food systems:**
  - gravimetric methods (desiccators)[2]
  - dynamic gas phase (IGC) technique[3-5]

1. O'Neill, In *Flavor-food interactions*; 1996. ACS: Washington, DC.; pp 59-74.
2. Thanh *et al*., *Food Chem*. 1992, *43*, 129-135.
3. Aspelund, T. & Wilson, L. *J. Agric. Food Chem*. 1983, *31*, 539-545.
4. Boutboul *et al*., *Food Chem*. 2000, *71*, 387-392.
5. Zhou and Cadwallader, *J. Agric. Food Chem*. 2004, *52,* 6271-6277.

What is IGC ?

- **Molecular probe technique for characterizing solid matrices**
- **IGC versus conventional GC**
  - **Same principle**
  - **Inversed phases**



known

unknown

* Drawing adapted from http://www.smsuk.co.uk/products_igc_technique.html

What can IGC do?

Thermodynamic measurements

- **thermodynamics of adsorption (*ΔH*, *ΔG* , *ΔS*)**

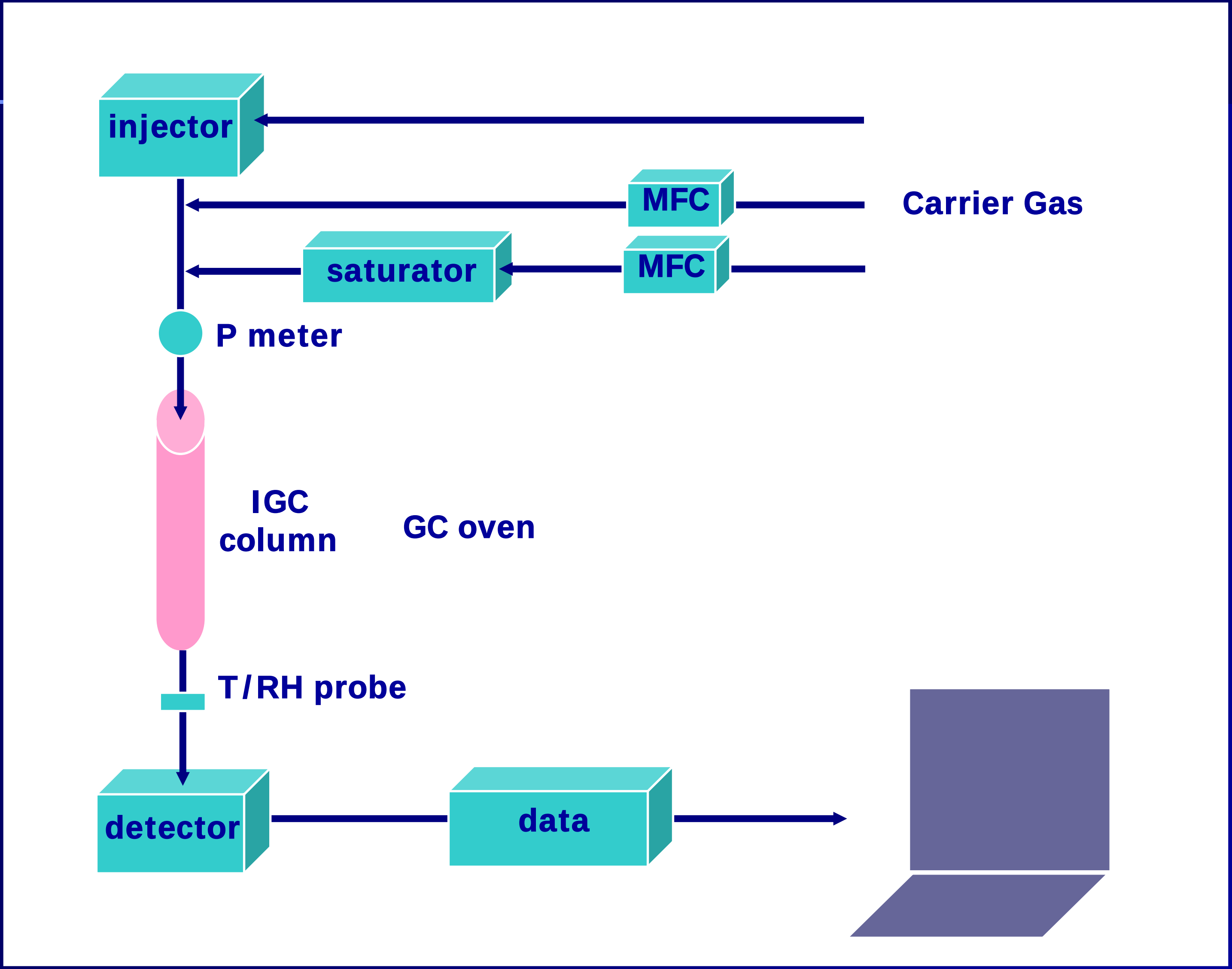
  interaction strength and binding affinity
- **glass transition temperature (T_g)**
- **surface energy**

Other

- **(flavor) sorption isotherms**

  surface chemistry of the sorbent
- **diffusion and partition**
- **crystallinity . . .**

IGC system developed in our lab . . .



injector

MFC

Carrier Gas

saturator

MFC

P meter

IGC column

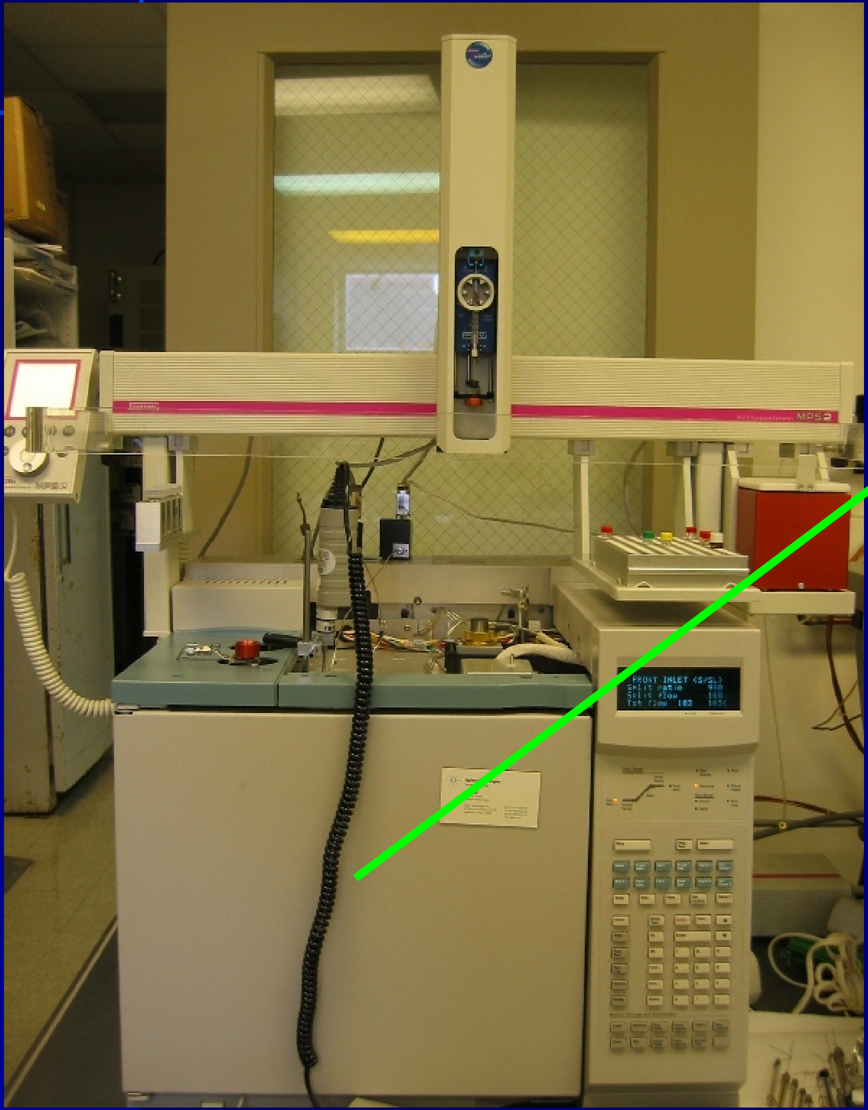
GC oven

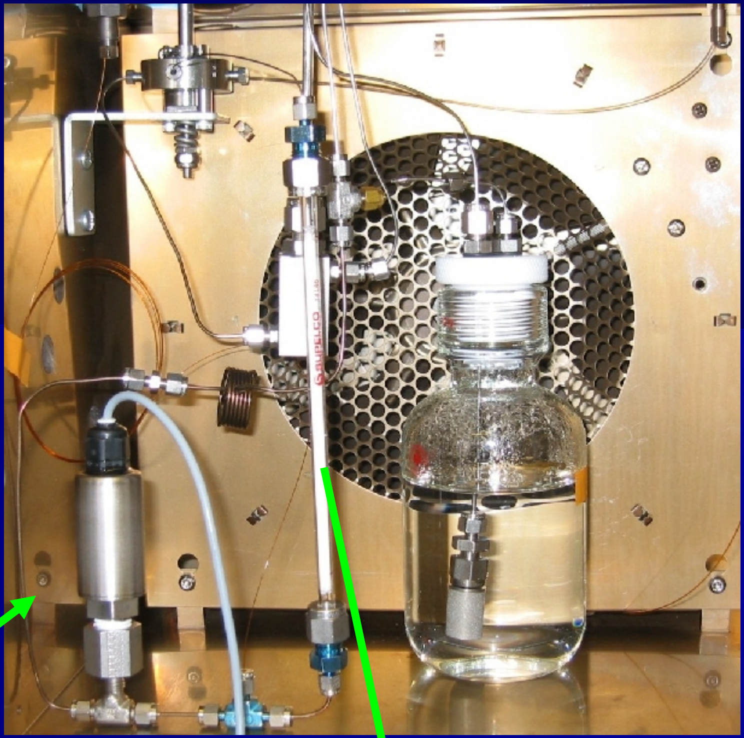
T/RH probe

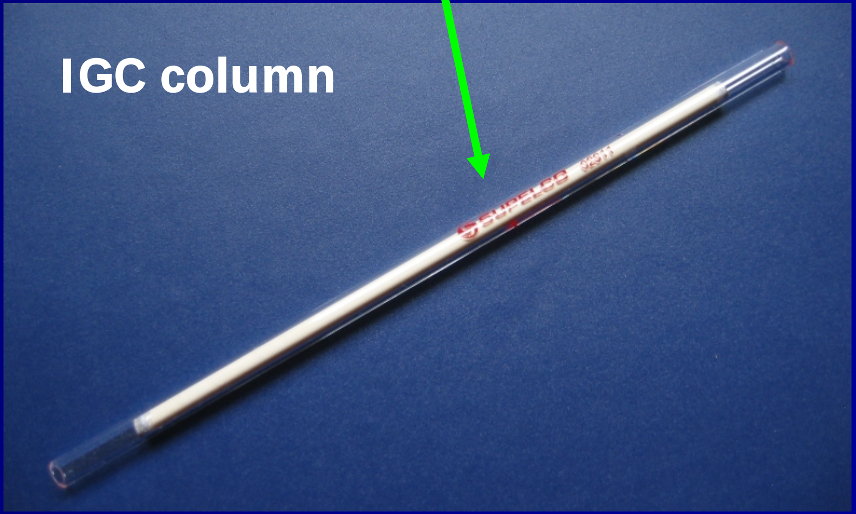
detector

data

IGC System



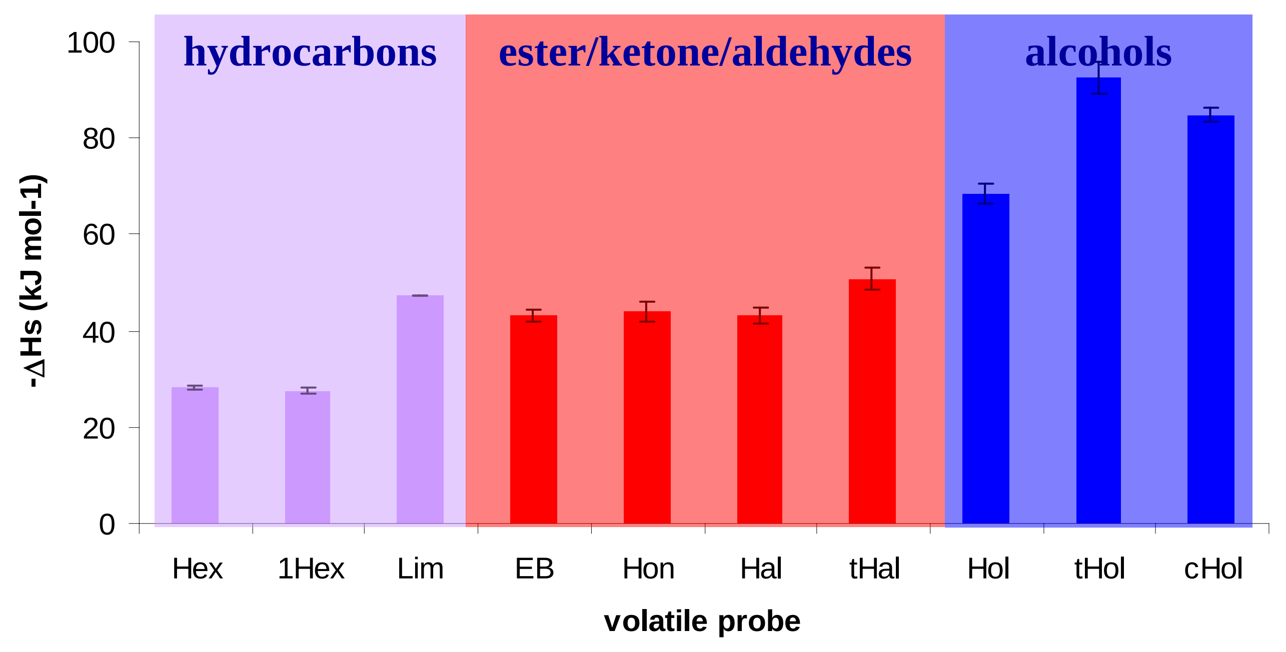




IGC column

Soy Protein Selectively Binds Volatile Flavor Compounds

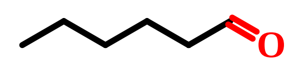
At 0 % RH, functional group determines binding force (*enthalpy of adsorption*)

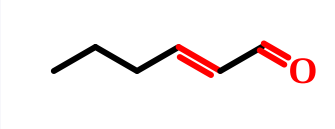


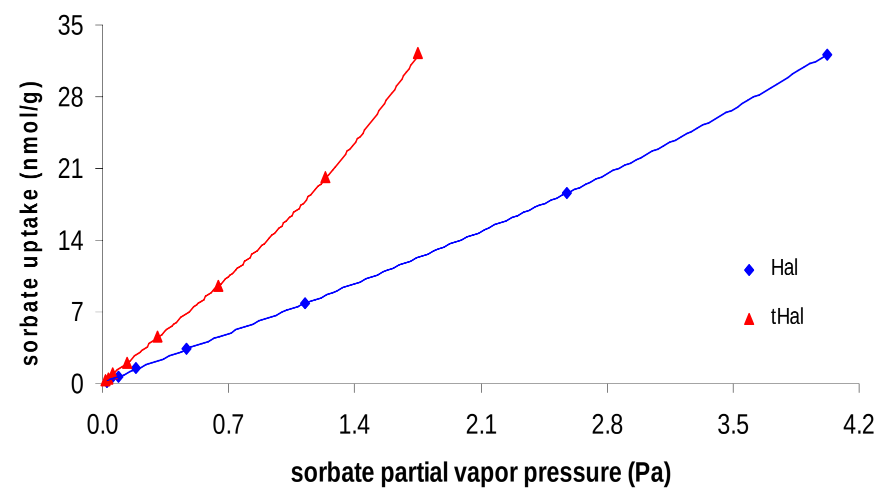
- **hydrocarbon/terpene: weak interacting compounds**
- **ester/ketone/aldehyde: medium/strong interacting compounds**
- **alcohols: strong interactions**

Effect of conjugated double bond . . .

hexanal vs ***trans*-2-hexenal**



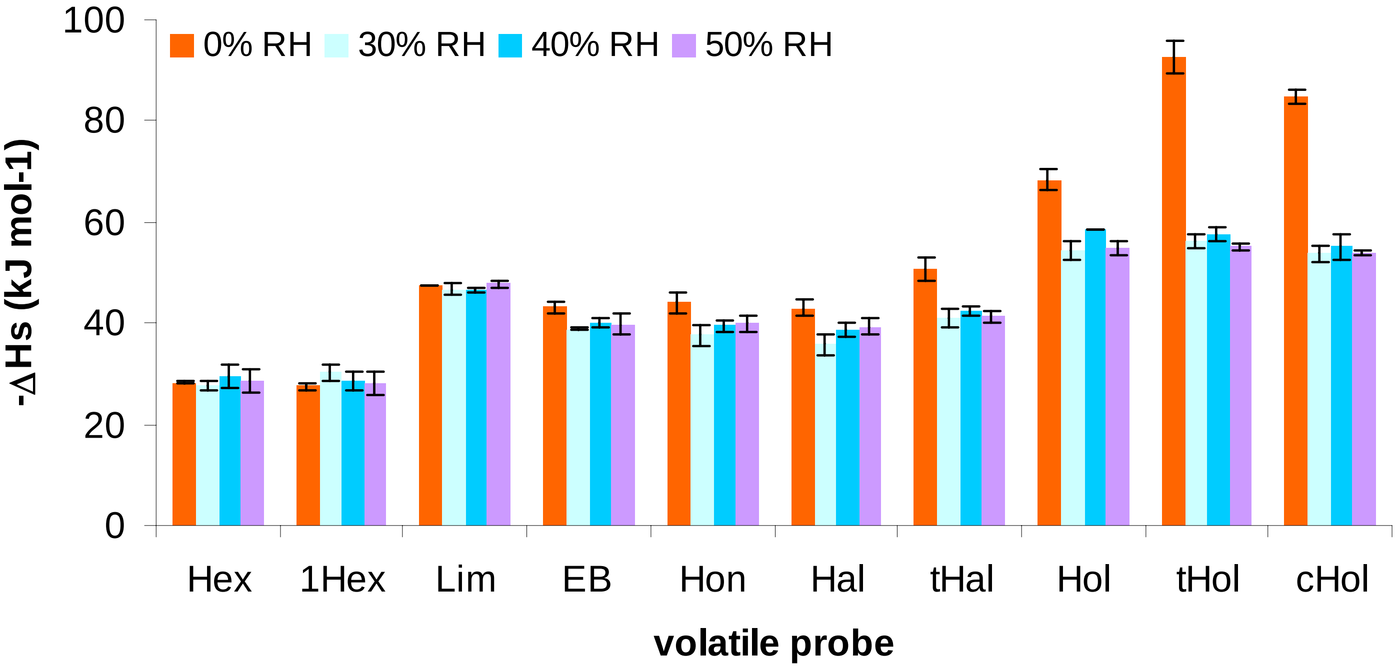




	$-\Delta H_s$ (kJ mol^{-1})
Hal	**43.0**
tHal	**50.8**

Isotherms determined for hexanal and *trans*-2-hexenal at 35 °C and 0 % RH.

Water is a strong competitor for polar binding sites

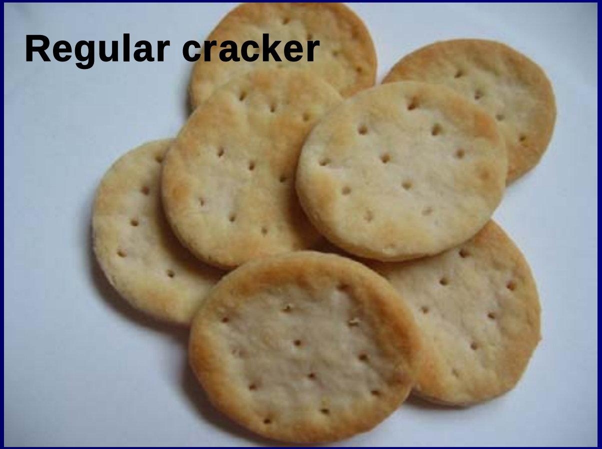


- functional group is important at each RH evaluated
- polar compounds: binding strength decreased → polar forces
- hydrocarbons: not affected → non-polar in nature

Can IGC give useful information in a REAL food system?

Binding of selected "butter" flavor compounds by soy-wheat soda cracker model systems

- Model food systems
  - regular wheat cracker
  - soy-wheat cracker (25% flour substitution)
- IGC measurements
  - flavor binding measured at 15% RH
  - volatile probes – diacetyl, butyric acid, γ-butyrolactone, hexanal



Regular cracker

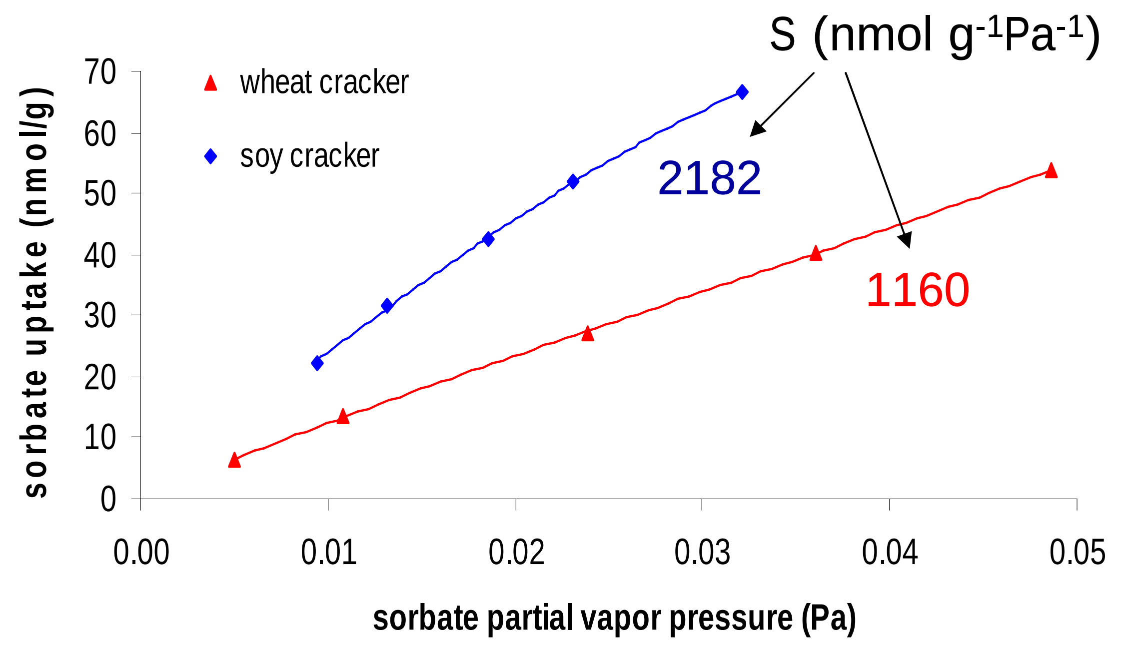
Soy enhanced cracker

IGC results . . .

- diacetyl binds to the two crackers with similar strength

	$-\Delta H_s$ (kJ mol^{-1})	
	wheat cracker	soy cracker
diacetyl	29.6 ± 0.2	29.1 ± 0.4
hexanal	35.7 ± 0.4	35.6 ± 0.1
γ-butyrolactone	45.4 ± 0.2	49.3 ± 0.2
butyric acid	57.3 ± 2.5	69.3 ± 0.9

- butyric acid has higher affinity to soy cracker



Is there an impact on sensory difference?

- Two compounds studied
  - diacetyl (1.3 mg/30 g cracker)
  - butyric acid (2.9 mg/30 g cracker)

- Orthonasal evaluation
  - 2-AFC (paired comparison) with warm-up*
  - panelists identify the stimulus (stabilizes the concept) prior to difference testing

* O'Mahony et al., The warm-up effect as a means of increasing the discriminability of sensory difference tests. *J. Food Sci.* 1988, *53,* 1848-1850.

sensory results demonstrate . . .

In terms of headspace aroma intensity of the two crackers:

- **for diacetyl: NO difference was found**

  $p < 0.2232$; estimated probability = 0.5333; power = 0.188

- **for butyric acid: significantly different**

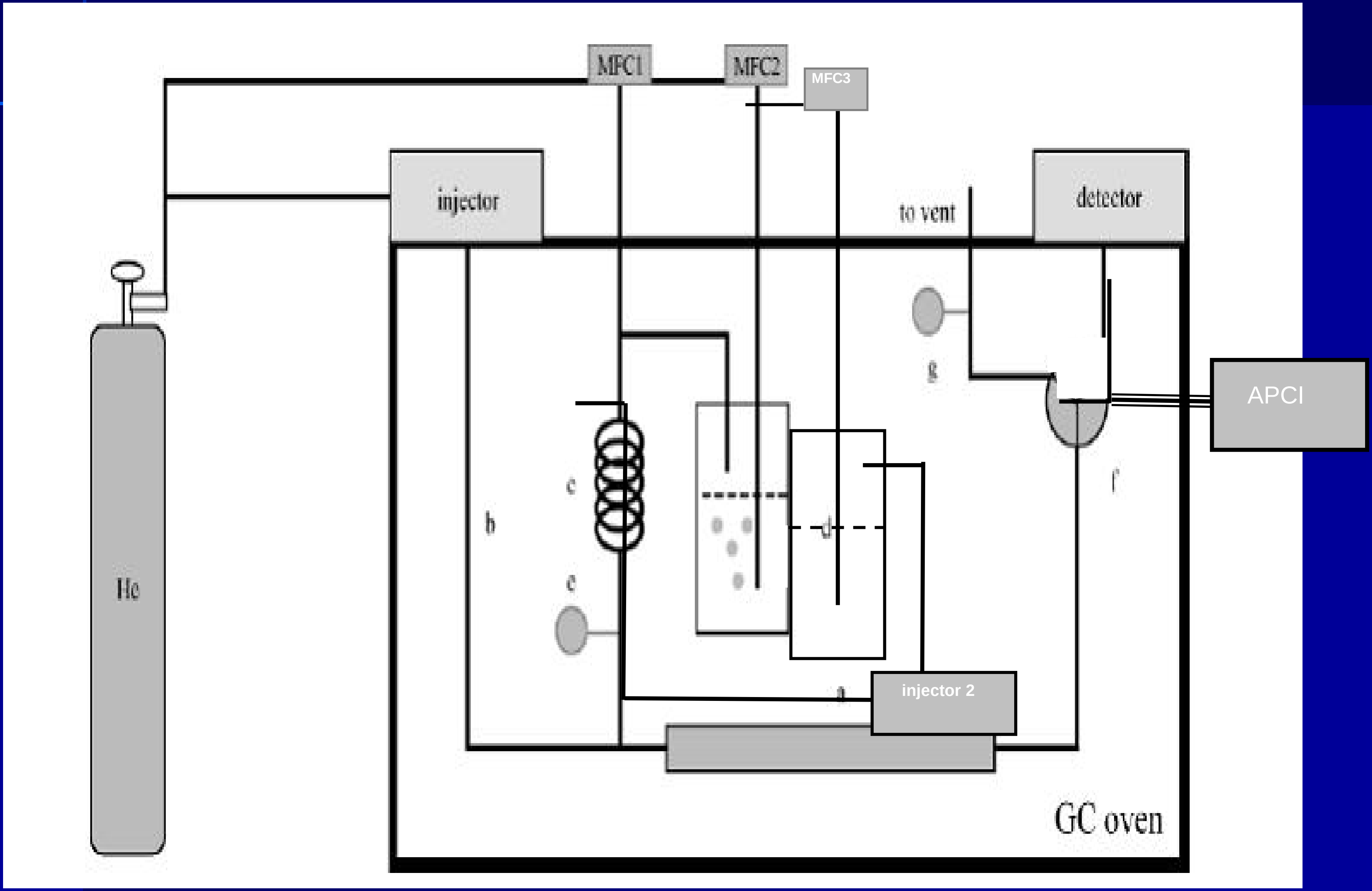
  $p < 0.0001$; estimated probability = 0.6333; power = 0.915

*** Based beta-binomial statistics [IFPrograms Software (null probability = 0.05)]**

Current Studies

- Multiple interactions between volatile compounds (VOC) and the matrix are found in real foods.
- Our aim is to assess the interactions between multiple VOCs (binary mixtures) and SPI in low moisture in real time
- Approach – use IGC-APCI-MS with dual vapor generators for simultaneous control of competitor VOC and relative humidity.

IGC-w/ APCI detection



Summary and Conclusions

- IGC useful for characterizing flavor-matrix binding properties
- IGC data supported by sensory evaluation results
  - IGC data may help predict sensory impact
- Multiple compound studies may provide additional insights into mode(s) of binding/competition.

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