

# Recent Developments in Noninvasive Techniques for Food Internal Quality Analysis

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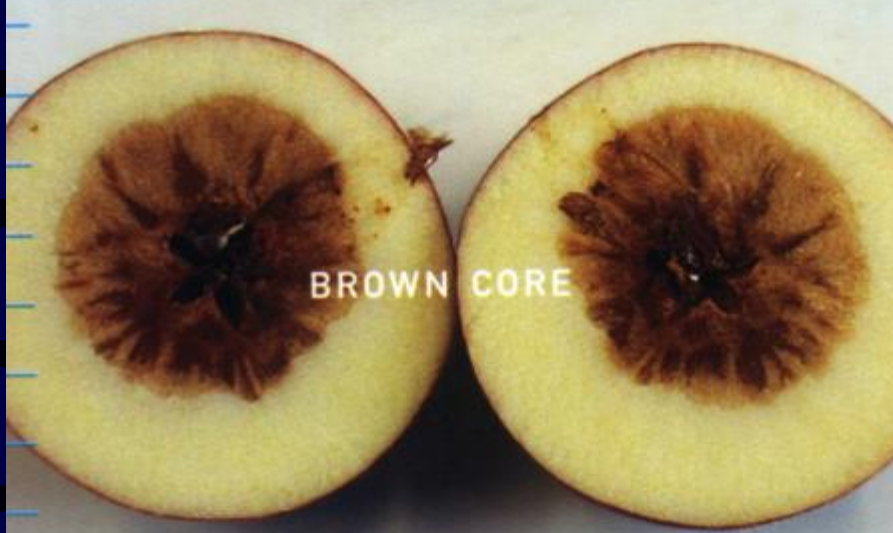
How does it look inside?



?



## Internal decay



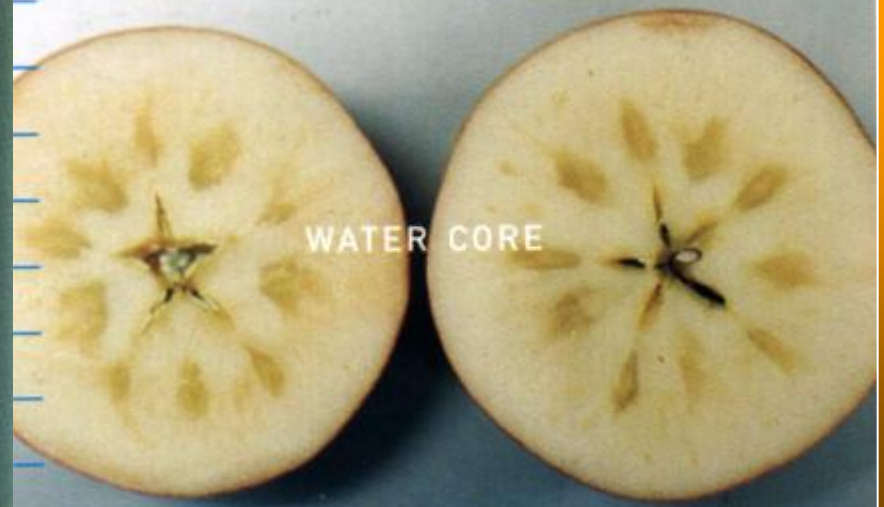
## CO<sub>2</sub>-decay



## internal browning



## water core



# Quality Parameters

## nondestructive measurement

- Surface colour
- Surface defects
- Size
- shape
- Rigidity
- Texture
- Density
- Ripeness
- Temperature defects
- Internal cavities
- Internal inclosures  
(Insects, particles)
- Physiol. losses, internal  
browning
- Chemical composition?
- Aroma?
- Flavour?



# Non Destructive Techniques

- Acoustical properties
- Dielectrical behaviour
- Optical imaging (colour, shape, size)
- Magnetical properties (MRI)
- Mechanical vibrations (pressure)
- Mikrowave (density, humidity)
- Light-reflexion, -transmission und –emission  
VIS/MIR/NIR
- X-Ray

# Sorting parameters:

- Brix-value (total soluble)
- Glucose ?
- Fructose ?
- Sucrose?
- Acids (total acids)
- Citric acid ?
- Malic acid ?
- Quinic acid ?
- Vitamin C ?
- Fibre
- Antioxidants ?
- Antimutagenes ?
- Secondary plant compounds ?
- Ripeness
- Water core
- Internal defects

# Recent applications

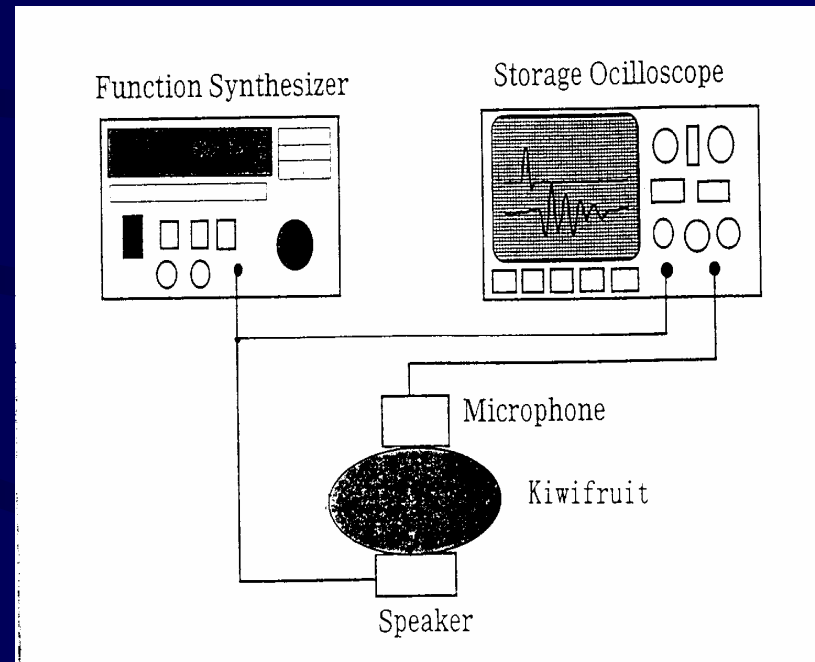
- Pears, apples, melons: Brix and firmness with VIS-NIR
- Pine apples: fresh-cut fruit „fresh and old“ NIR/MIR
- Mango, Banana, peach: firmness, combination VIS-NIR with acoustical impulse technique
- Beef: tenderness with Vis-NIR imaging
- Grapes: brix, fructose, pH-value, acidity
- Turkey, cut meat, classification



# Firmness measurements

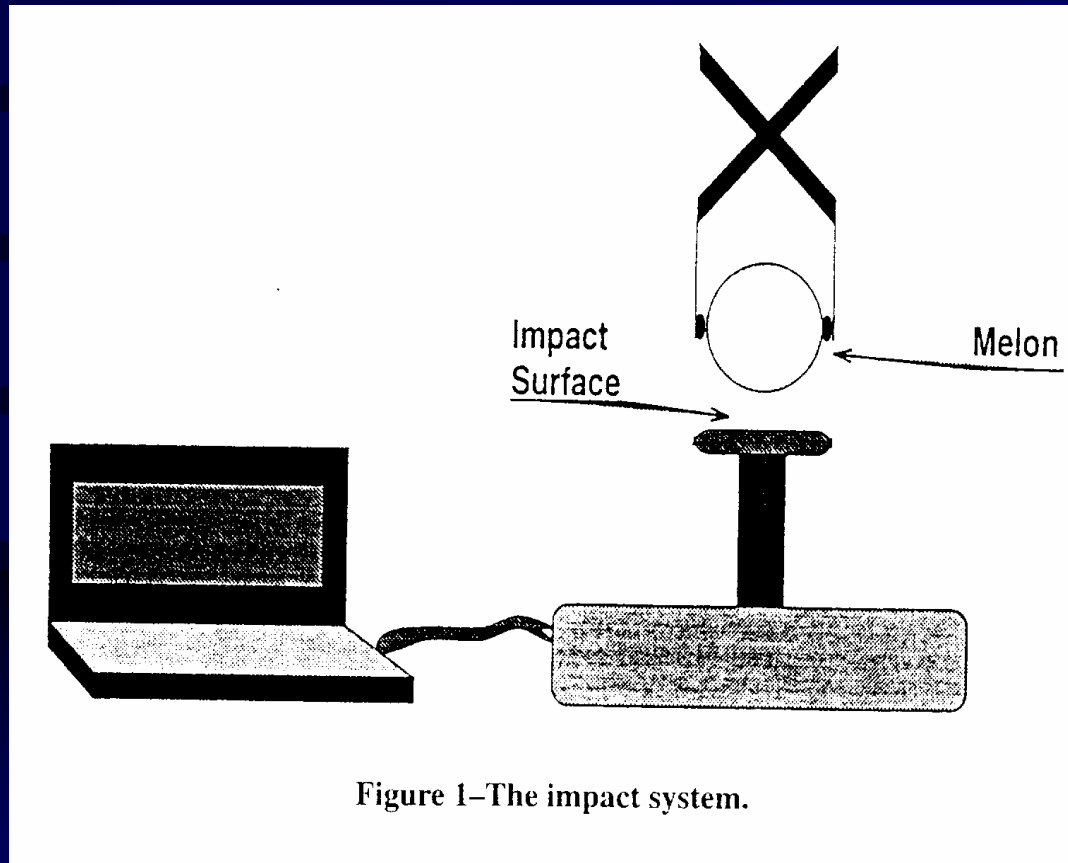
(super sonic)

- Vibronational properties of fruit and vegetables
- (Ultra)-sonic or mechanical impulses between 0-3 KHz
- Resonance frequencies decrease with increasing ripeness. They are directly correlated to firmness, rigidity and hardness
- Good correlation to Magness-Taylor firmness
- Not applicable to soft fruit and stone fruit



# Firmness measurement

Mechanical impulses via impact systems



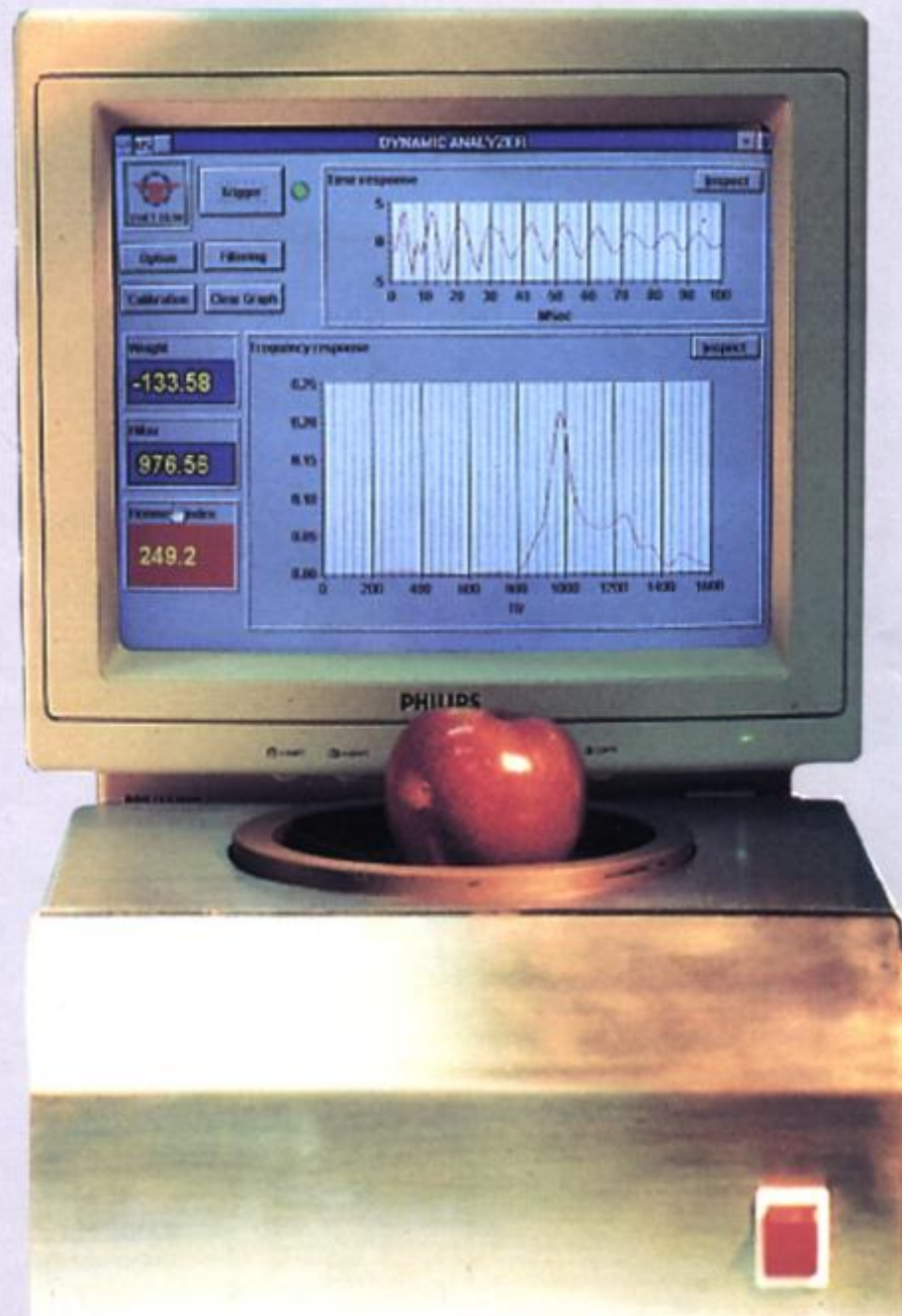




Fig. 5. A portable frequency response measurement instrument (<http://www.ava.co.jp>)

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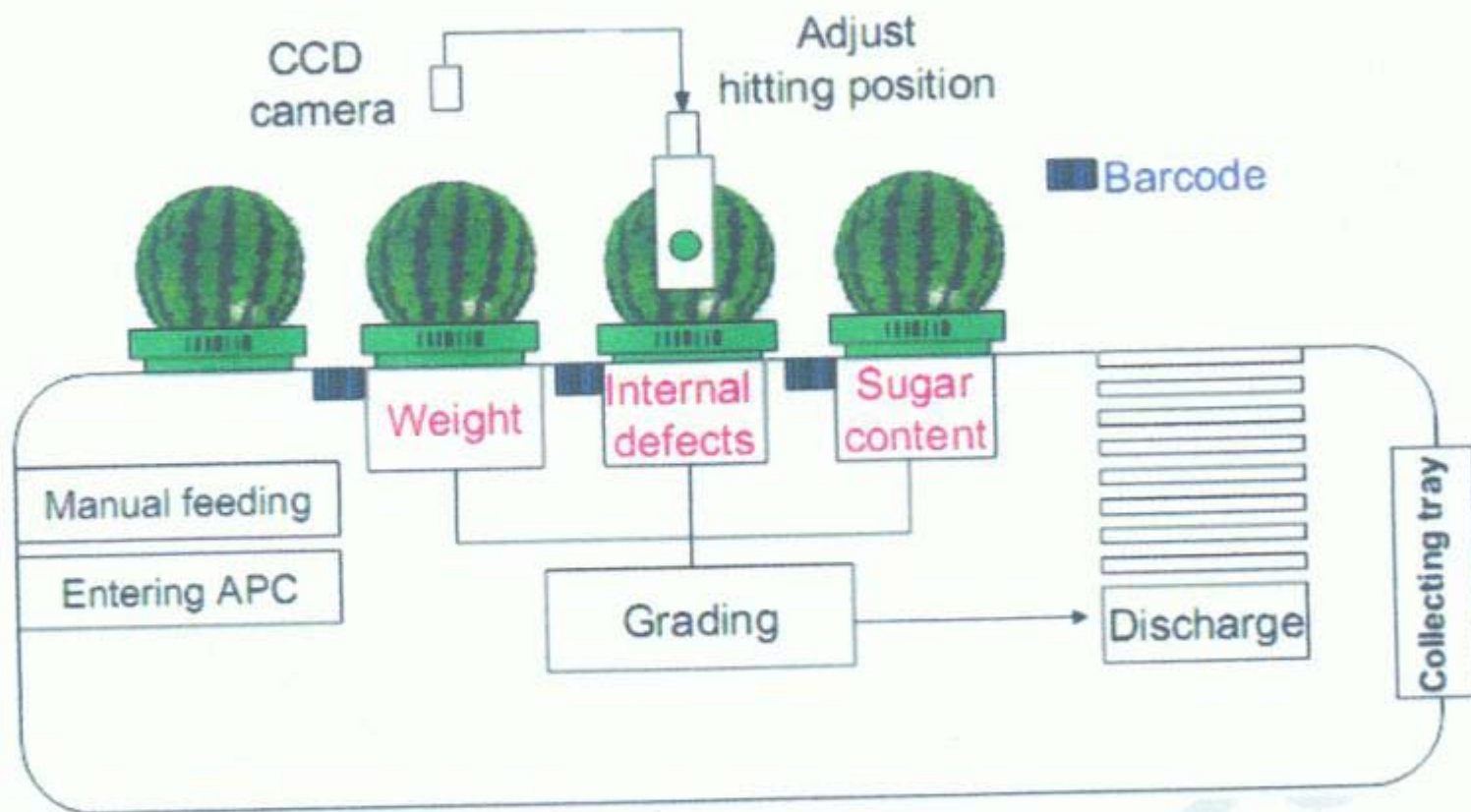


Fig. 9. Layout of the watermelon sorting system (Noh and Choi, 2006)



Fig. 8. Watermelon sorting system by acoustics technology  
(<http://www.shibuya-sss.co.jp>)

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# Nuclear Magnetic Resonance NMR

Magnetic properties of atoms (nucleons) in tissue

- Nuclear spin – magnetical moment
- This spins are in line in an external magnetic field (spin parallel or antiparallel)
- Äquilibrium being measured with radio frequency
- Signals spend informations about the chemical environment of the nucleons of concern

# NMR - techniques

## NMR-Imaging and other techniques

- Internal structure
- Fruit flesh browning
- Fat, sugar, water
- Ripeness
- Dry regions and dry weight

# NMR

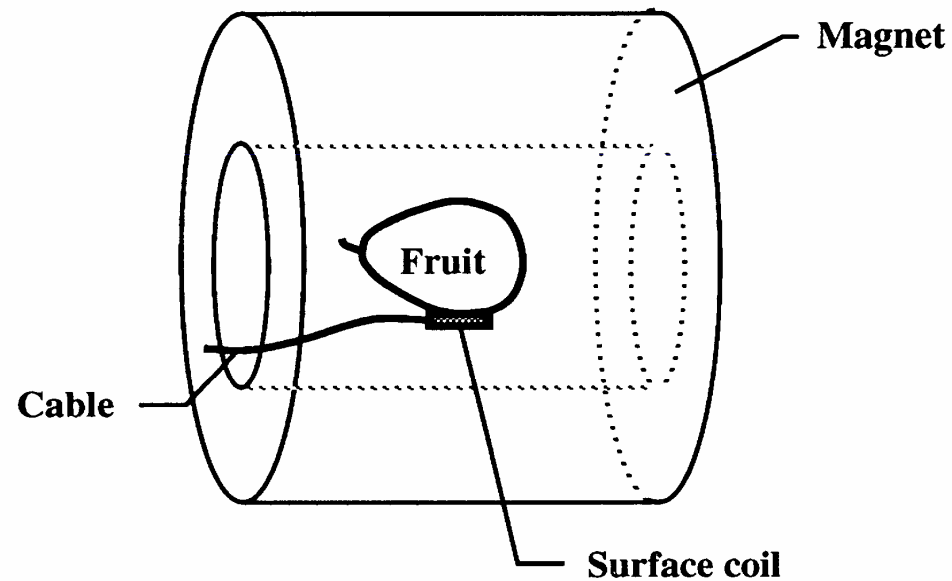


Figure 1. Schematic drawing showing the method used to measure NMR resonance peaks of an intact fruit using a 2 cm surface coil.

# NMR

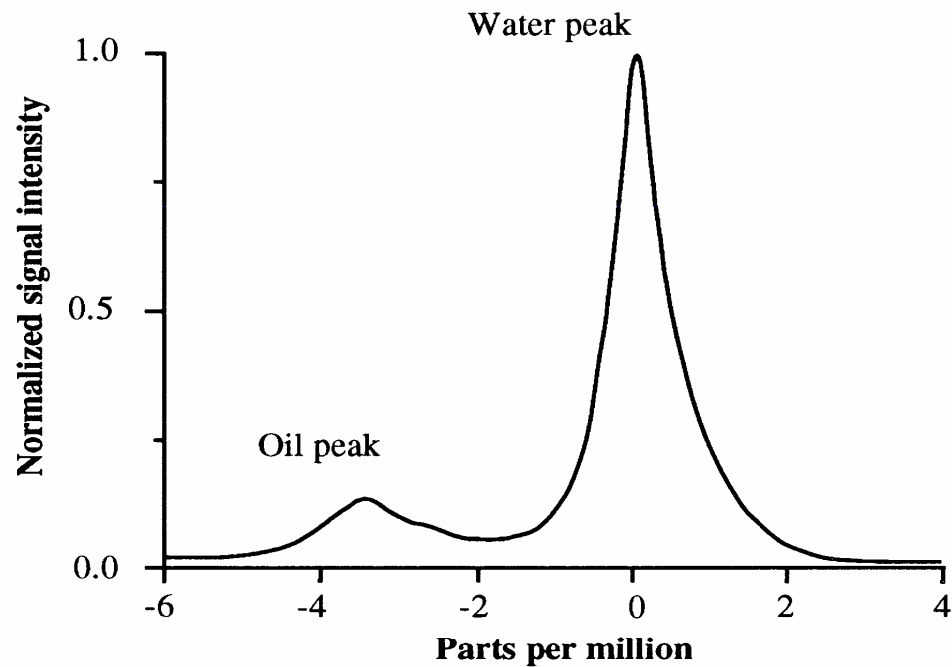
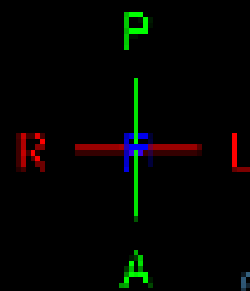
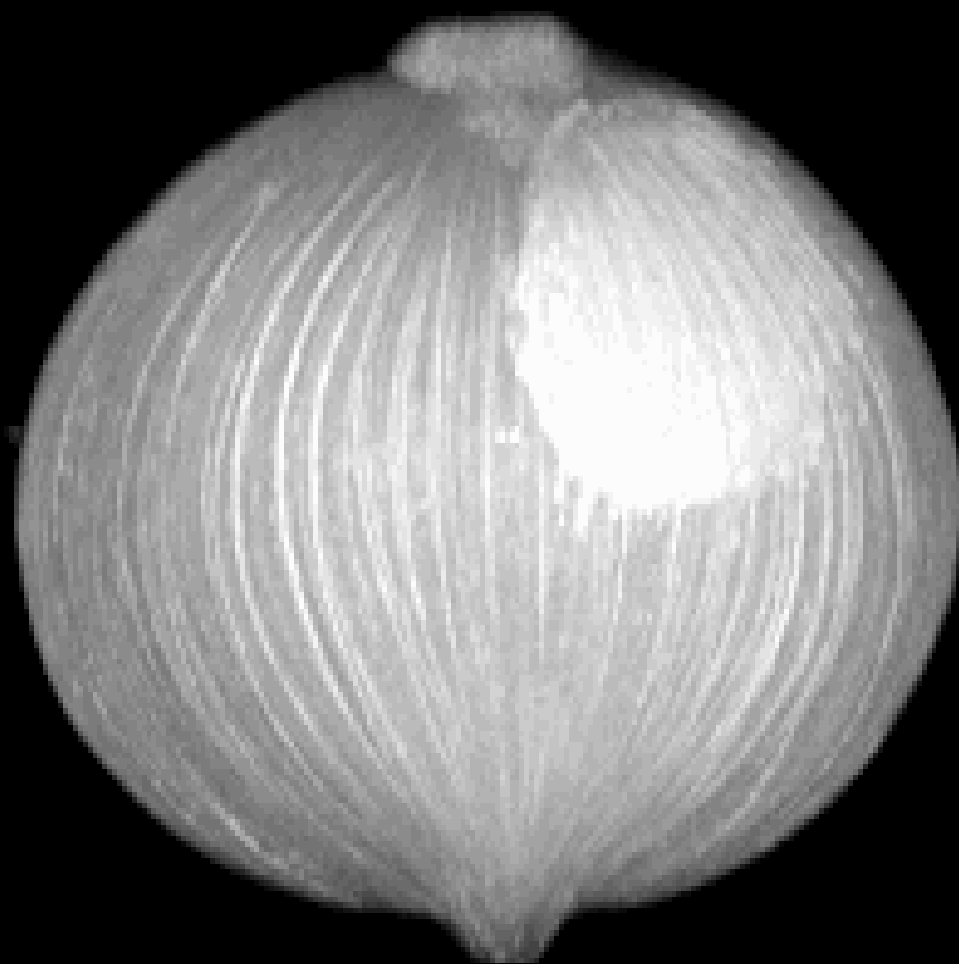


Figure 2. NMR spectrum of an avocado sample showing the resonance peaks of water and oil. The spectrum was acquired by placing the whole fruit against a 2 cm surface coil.



图 1-1-1







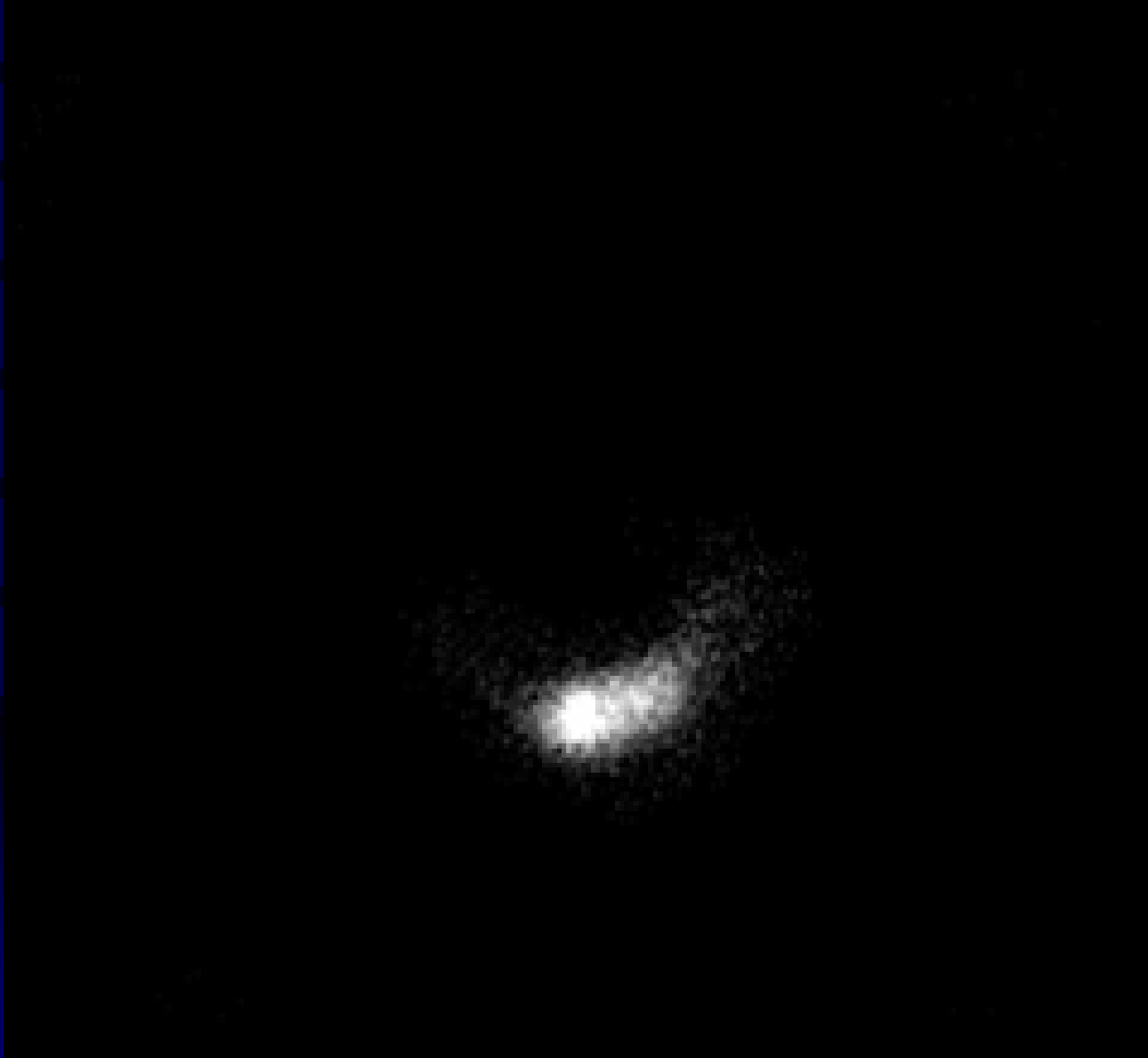
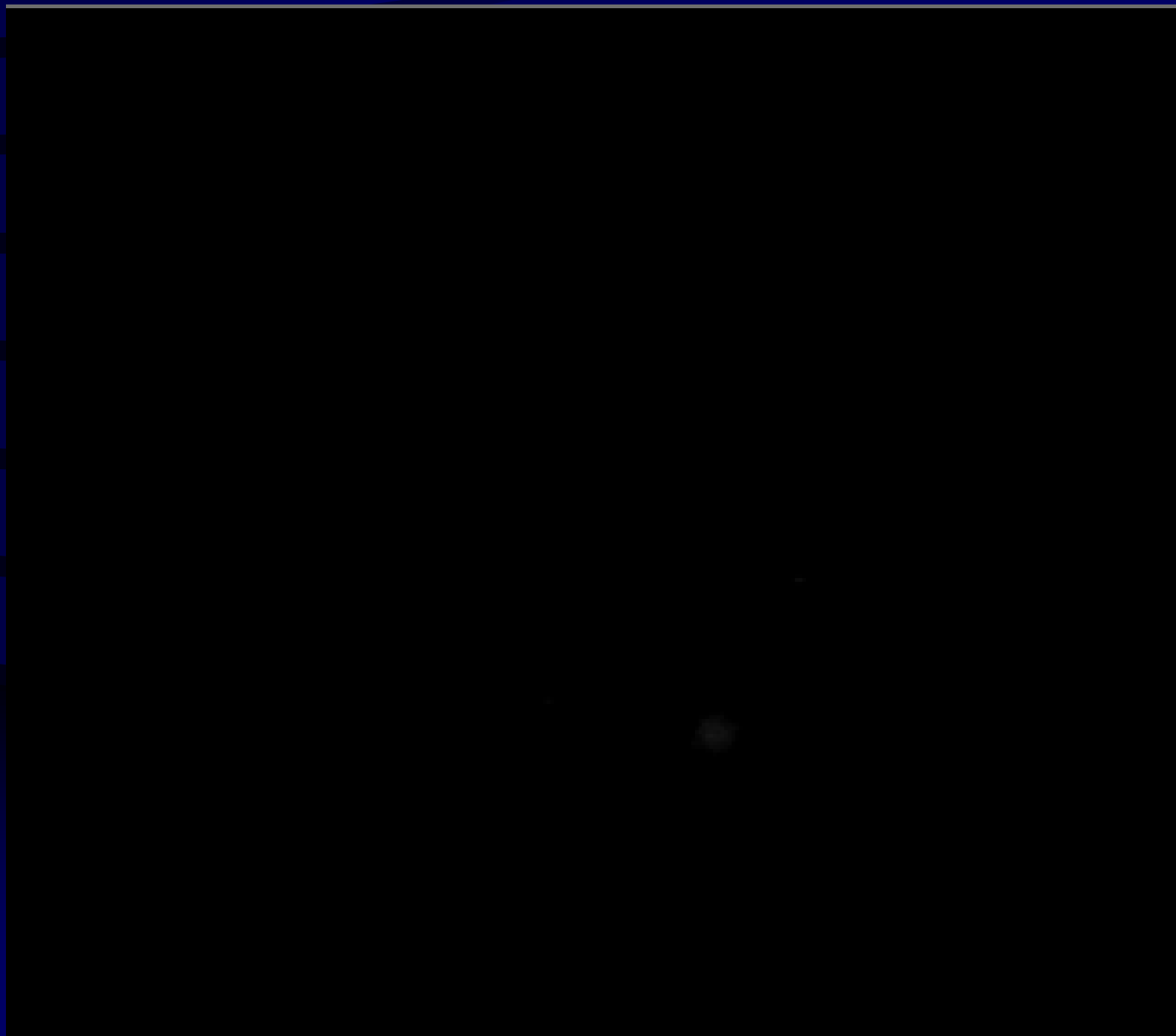




Figure 10.10

Two stars merging to form a black hole.



# Fluorescence and Delayed Light Emission (DLE)

Chlorophyll (ex. at 455 nm, 680 nm; em. at 650-750 nm, maximum at 690 nm, Shoulder at 735 nm)

- Fluorescence: photo system II, 1-3 sec, in tissue and in solutions
- DLE: only in intact chloroplasts, ms to min
- Ripeness, loss by heat and chill, physiological disorders

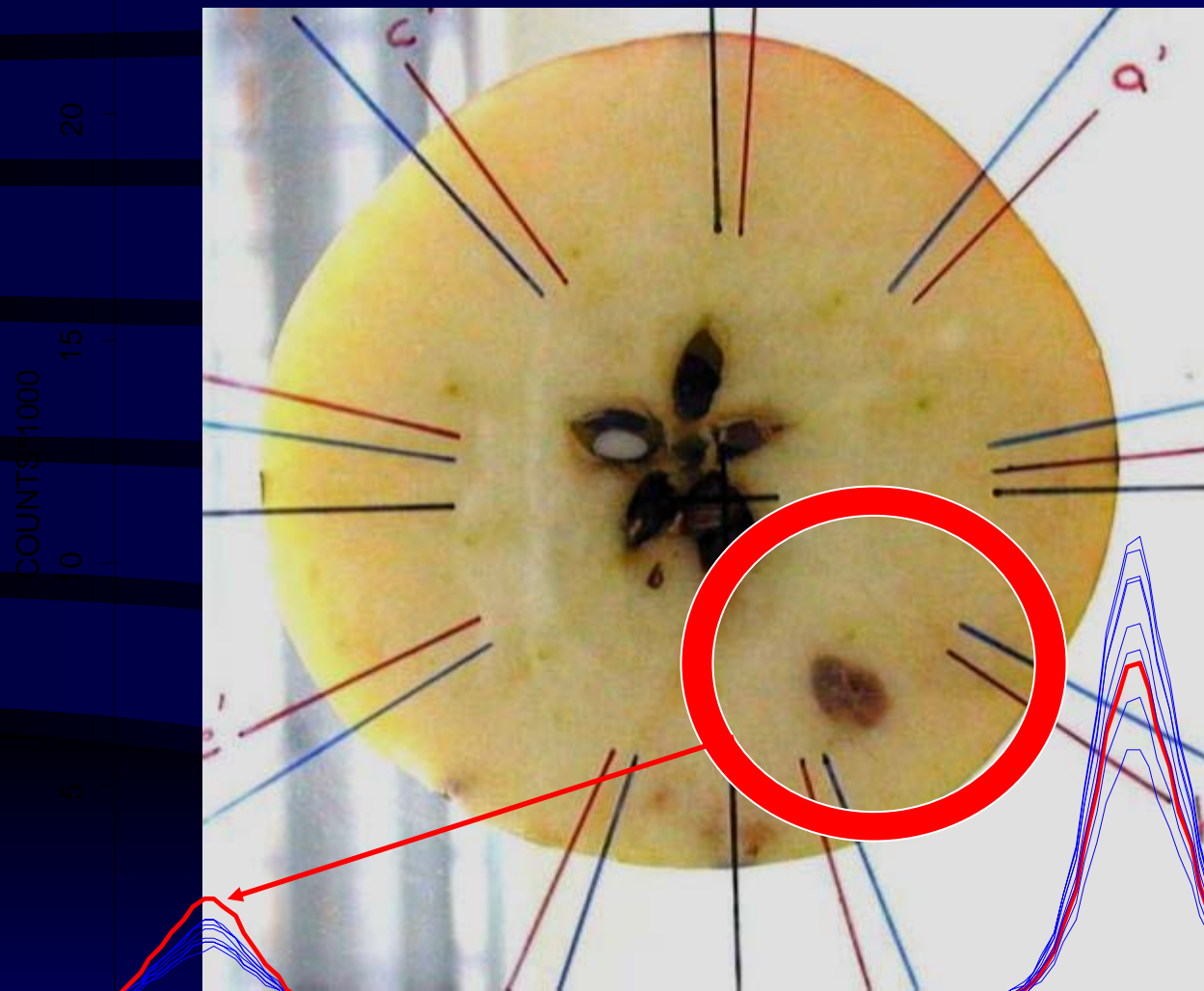
# X-ray Imaging

- Tissue damage in plant tissue
- Insects, internal defects (water core, fruit flesh browning, translucence in pine apples, chilling injuries, dry areas in orange
- Ripeness of peaches, mangoes, lettuce



# Near-Infra-Red-Spectroscopy

- UV/VIS: 100 – 750 nm
- NIR: 750 – 2500 nm (CH, OH, NH, over tones)
- MIR: >2500 nm
- Dry weight, proteins, sugars, acids, injuries like flesh browning, water inclusions, ripeness
- Japan, USA, NZ, Israel



COUNTS 1000

20

15

10

5

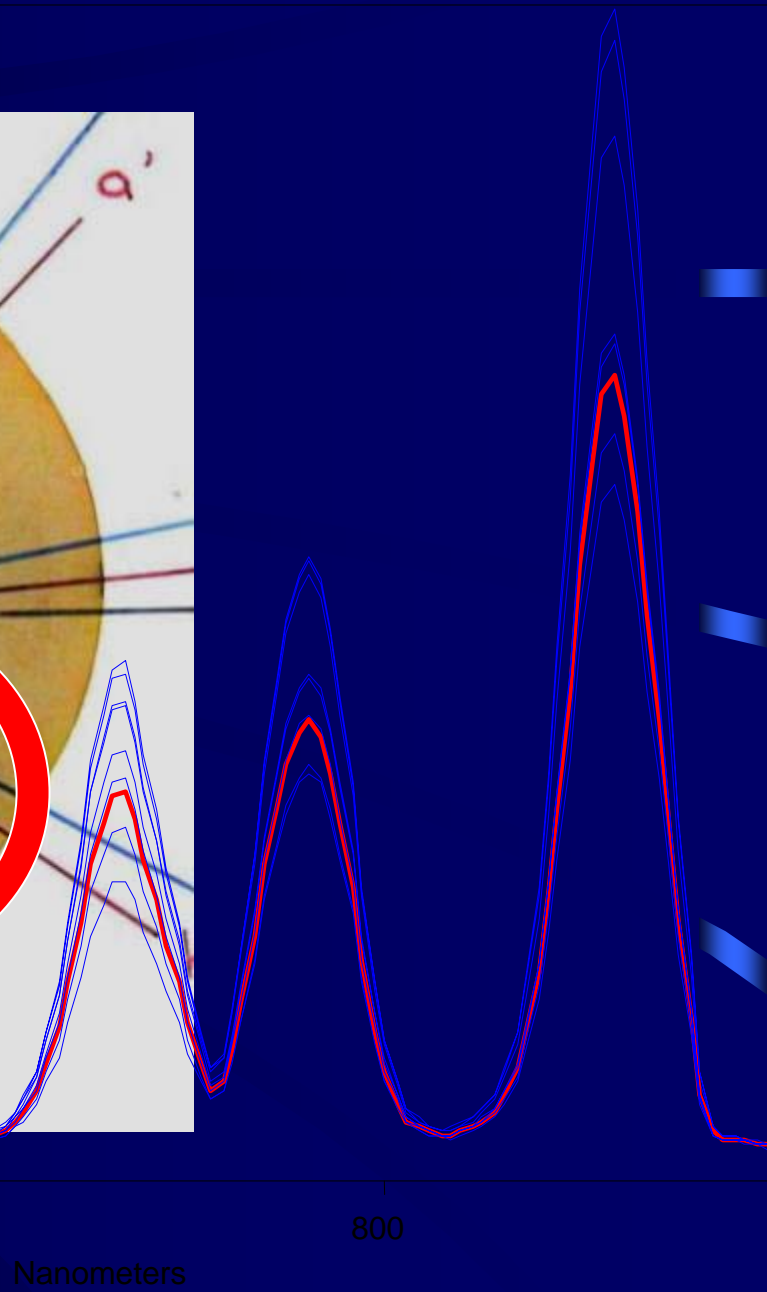
0

900

850

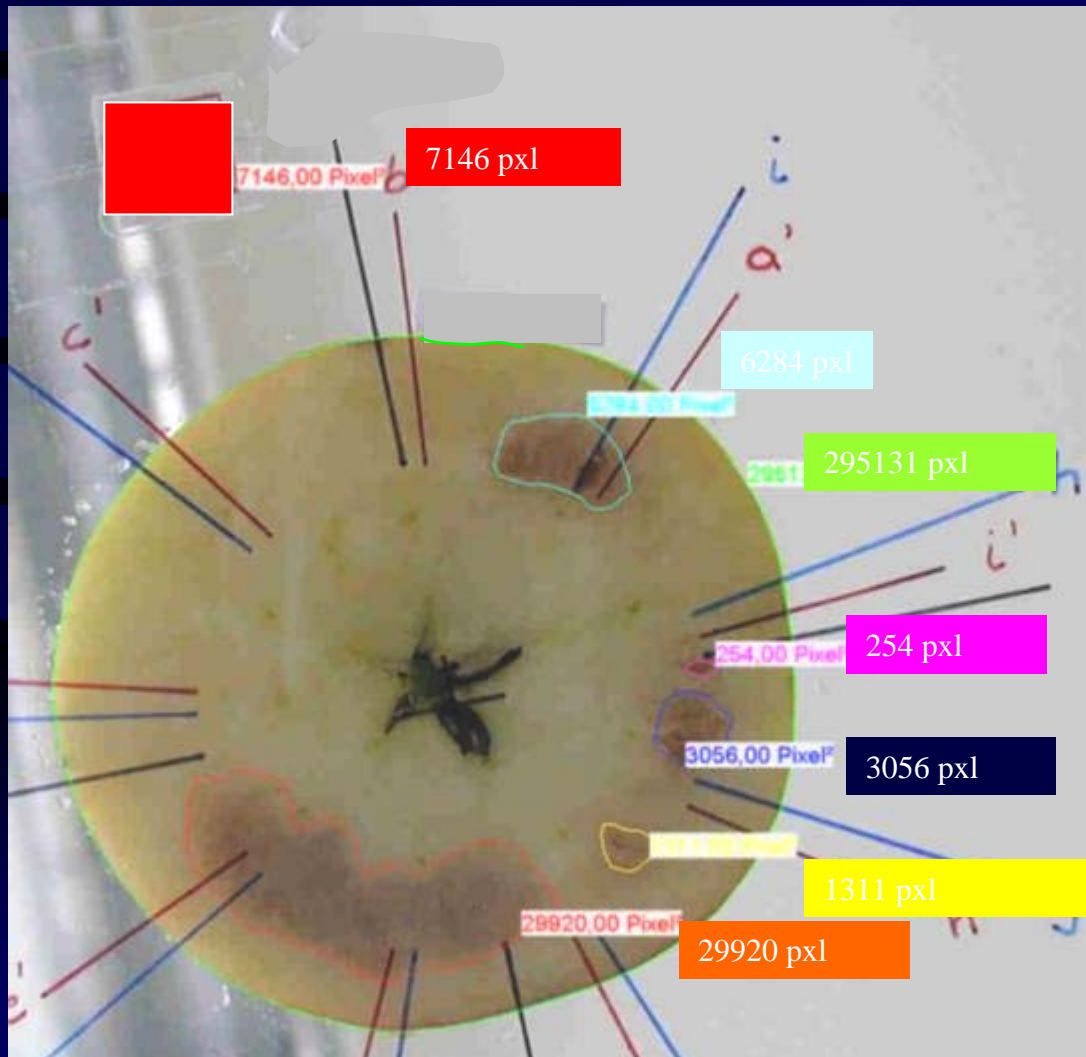
800

Nanometers



# NIR Diode Laser Non-Destructive Analysis

## Quantifying Defects using Image Recognition

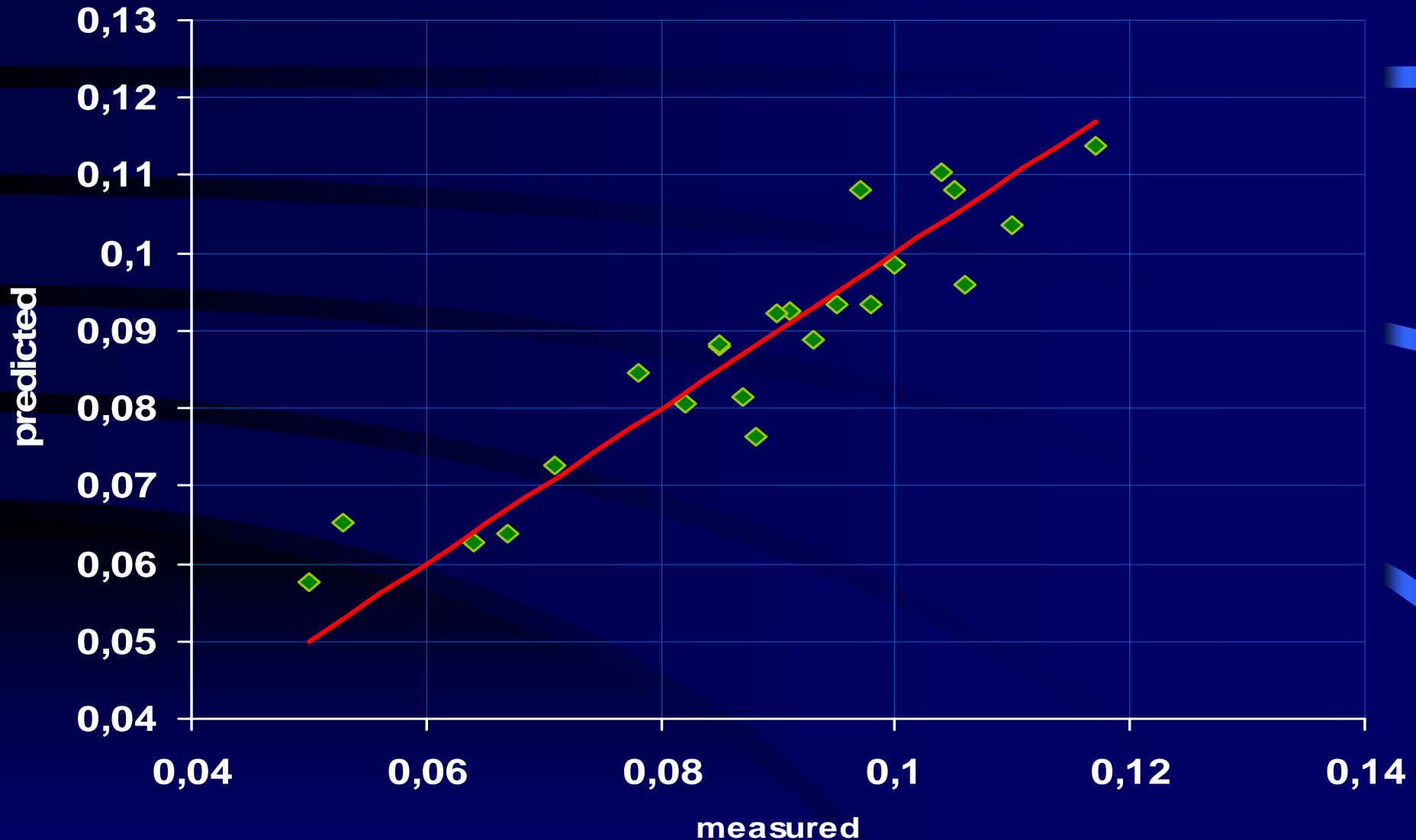


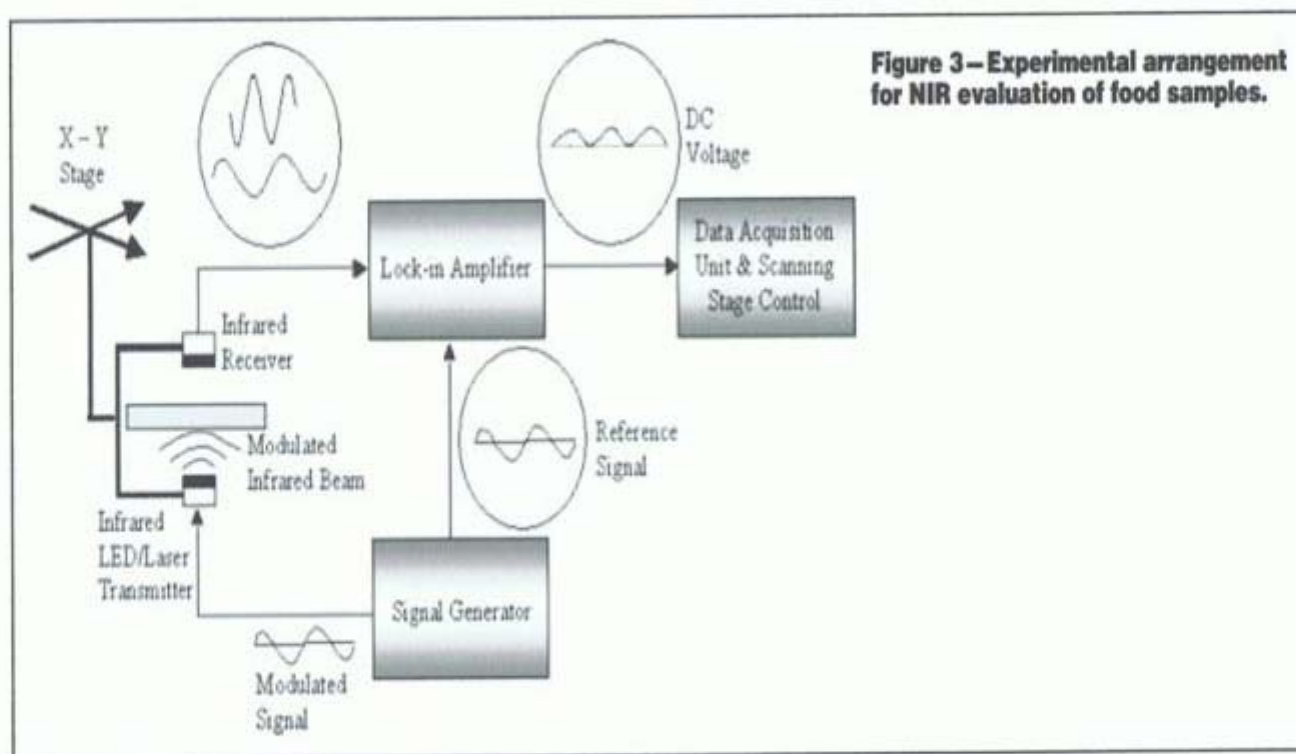
**$1 \text{ cm}^2 = 7146 \text{ pixel}^2$**

- Total defect area: 41000 pxl.
- Total apple area: 295000 pxl.
- **Relative defect area: 14 %**

- Defect classes:
- class 0: 0 %
- class 1: 0 – 5 %
- class 2: 5 – 10 %
- class 3: 10 – 25 %
- class 4: 25 – 50 %

# Fruit flesh firmness of apples





**Figure 3—Experimental arrangement for NIR evaluation of food samples.**

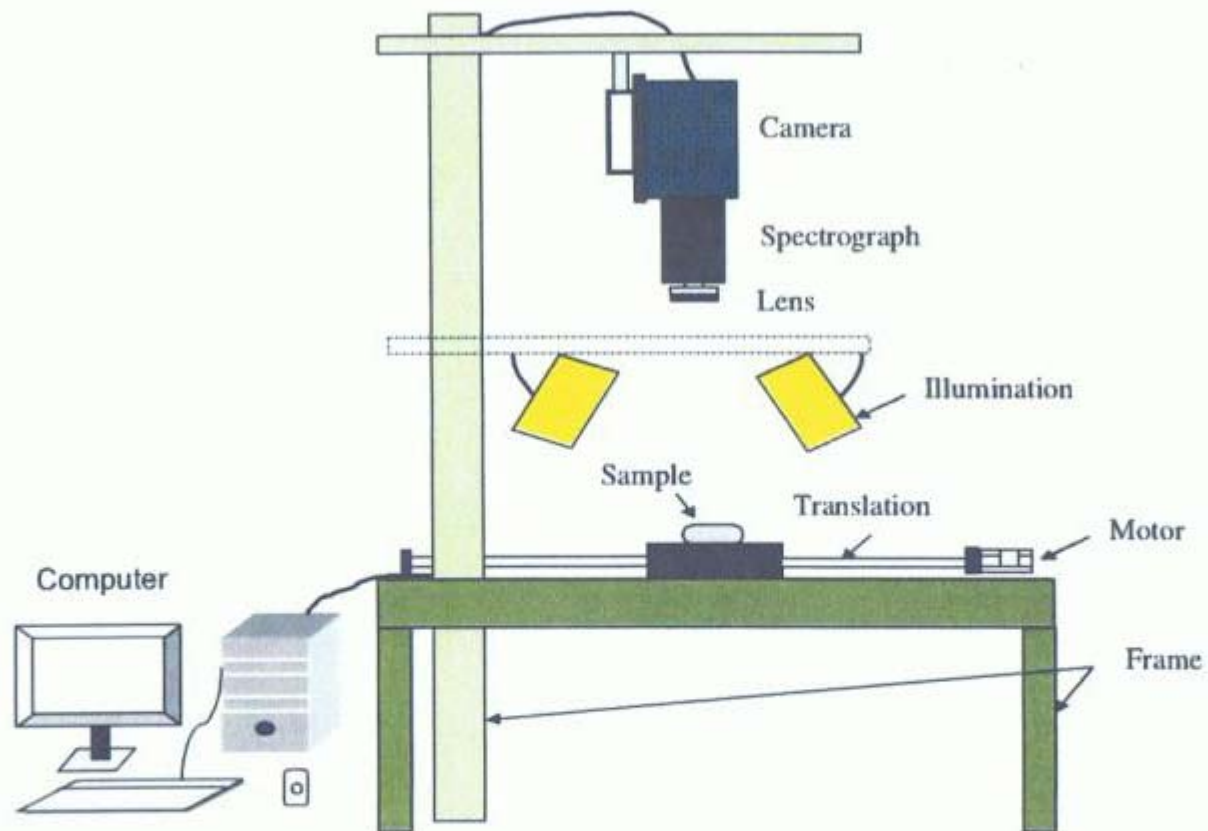
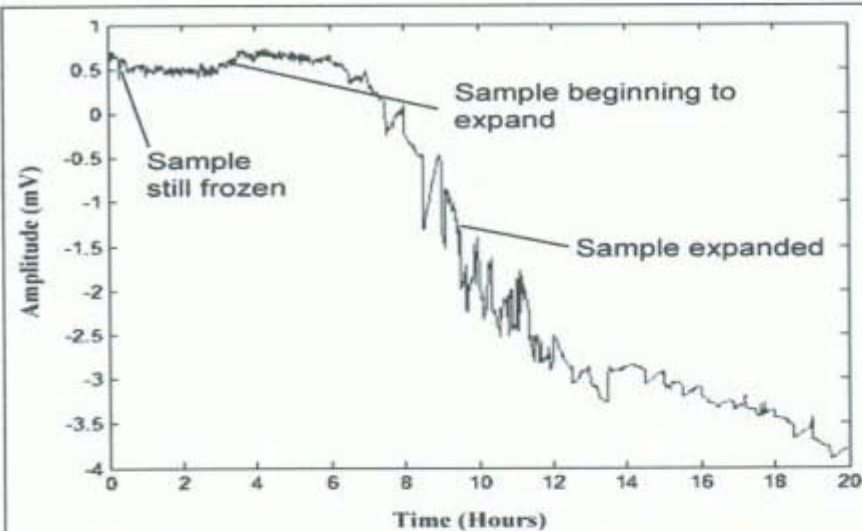
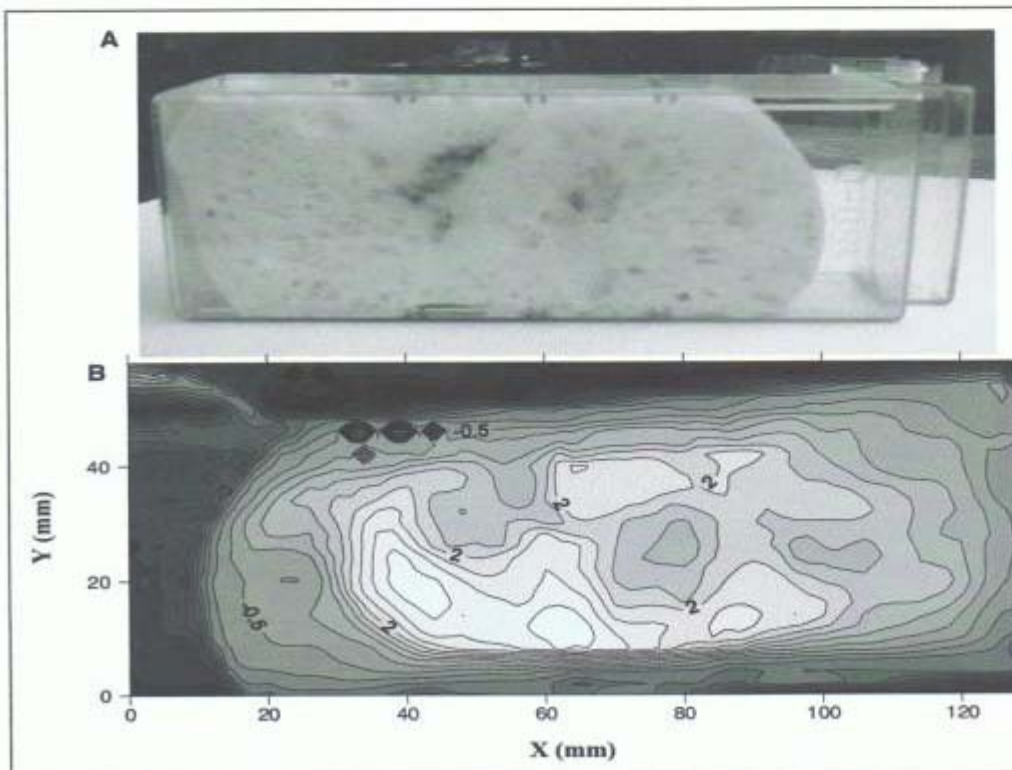


Fig. 1. Schematic diagram of the hyperspectral imaging system.

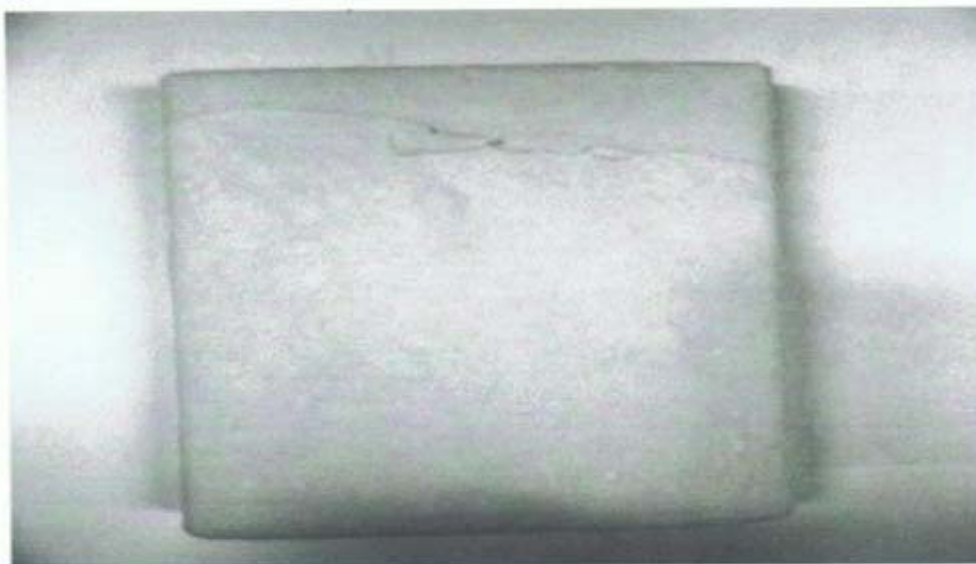
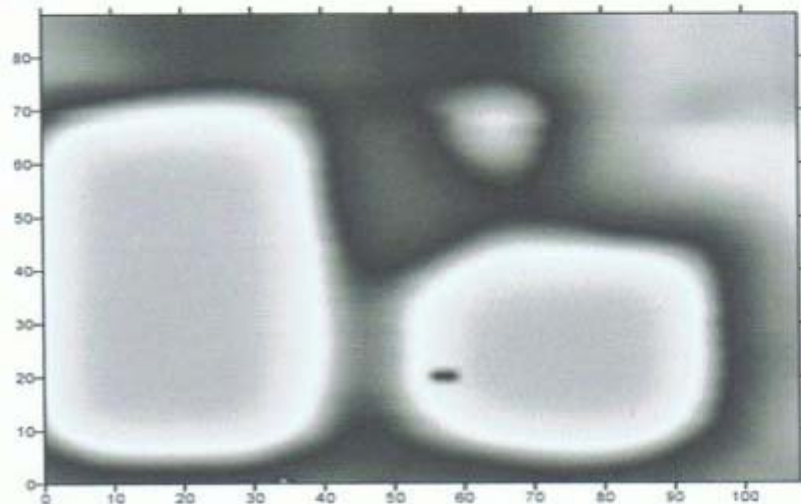




**Figure 4—Time-dependent change in through-transmitted NIR amplitude as a sample of frozen dough gradually thawed and expanded in a room temperature environment.**



**Figure 5—NIR scan of a risen dough sample containing air-pockets. (A) Conventional photograph of the specimen; (B) a NIR through-transmission image, with lighter areas representing lower transmission amplitudes.**

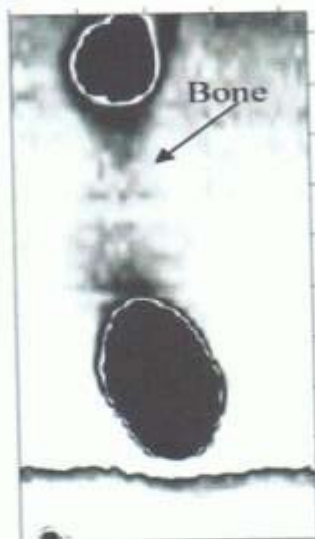
**A****B****C**

**Figure 8—(A) Conventional optical photograph of a pastry dough sample. (B) The NIR through-transmission image, showing detection of the objects that had been placed deliberately within the thickness of the sample (and which are shown in C). The coin is 24 mm in diameter.**

A



B

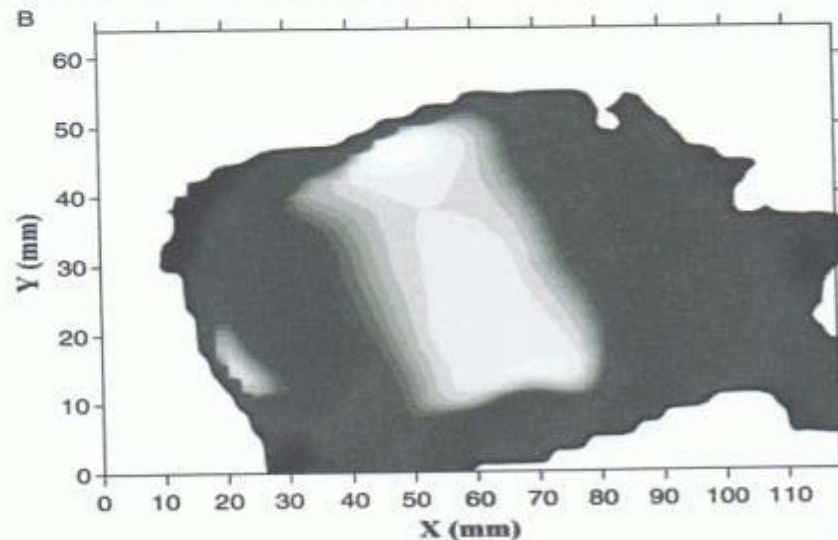


**Figure 11 — Images of a chicken “drum-stick” sample. (A) Conventional photograph, and (B) through-transmission NIR image showing the bone structure within the chicken. The darker areas are the thicker joints at either end, where the attenuation within the bone is greater.**

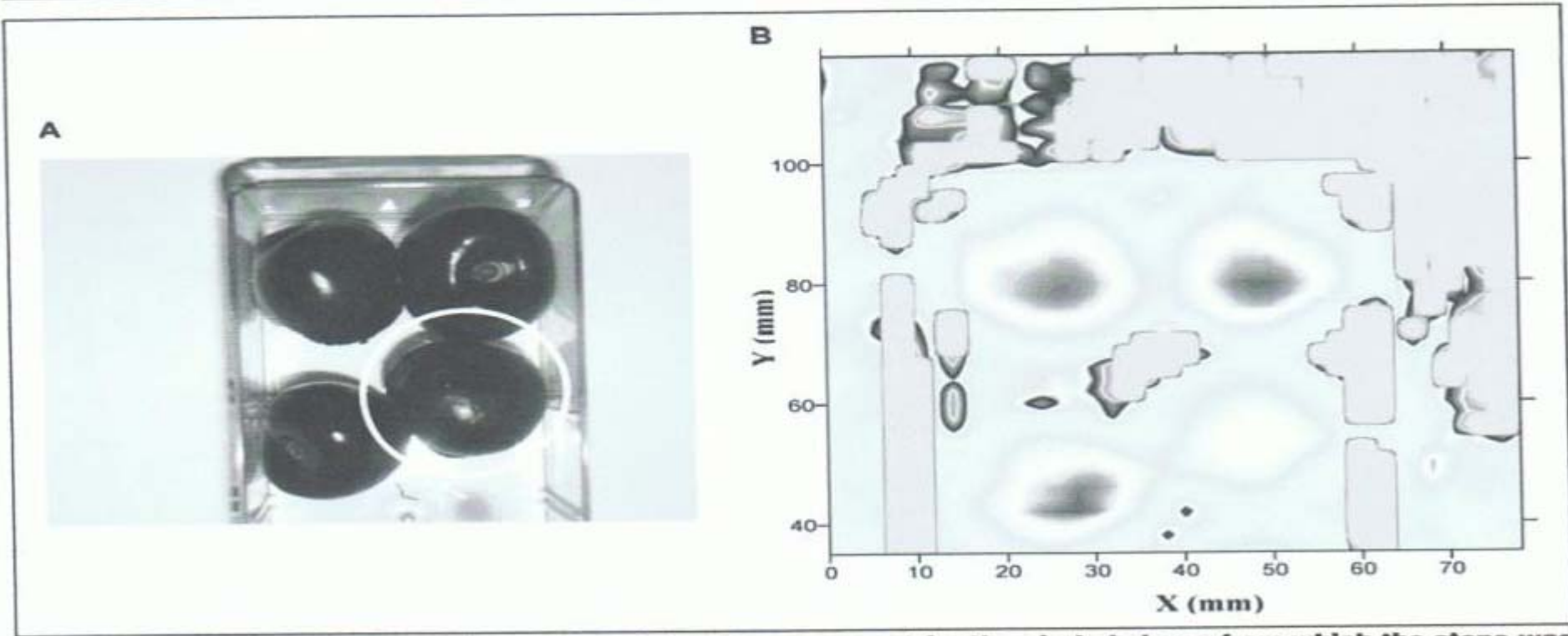
A



B



**Figure 12 — (A) Photograph of a strip of fat sandwiched between 2 layers of pork meat. (B) A NIR through-transmission image, in which the fat is clearly visible.**



**Figure 15 – (A) Photograph of 4 cherries containing stones, except for the circled cherry from which the stone was removed. (B) High-contrast NIR image, showing the detection of cherry stones as the darker areas, and the absence of a stone in the cherry at the bottom right.**





(Level 0)



(Level 1)



(Level 2)

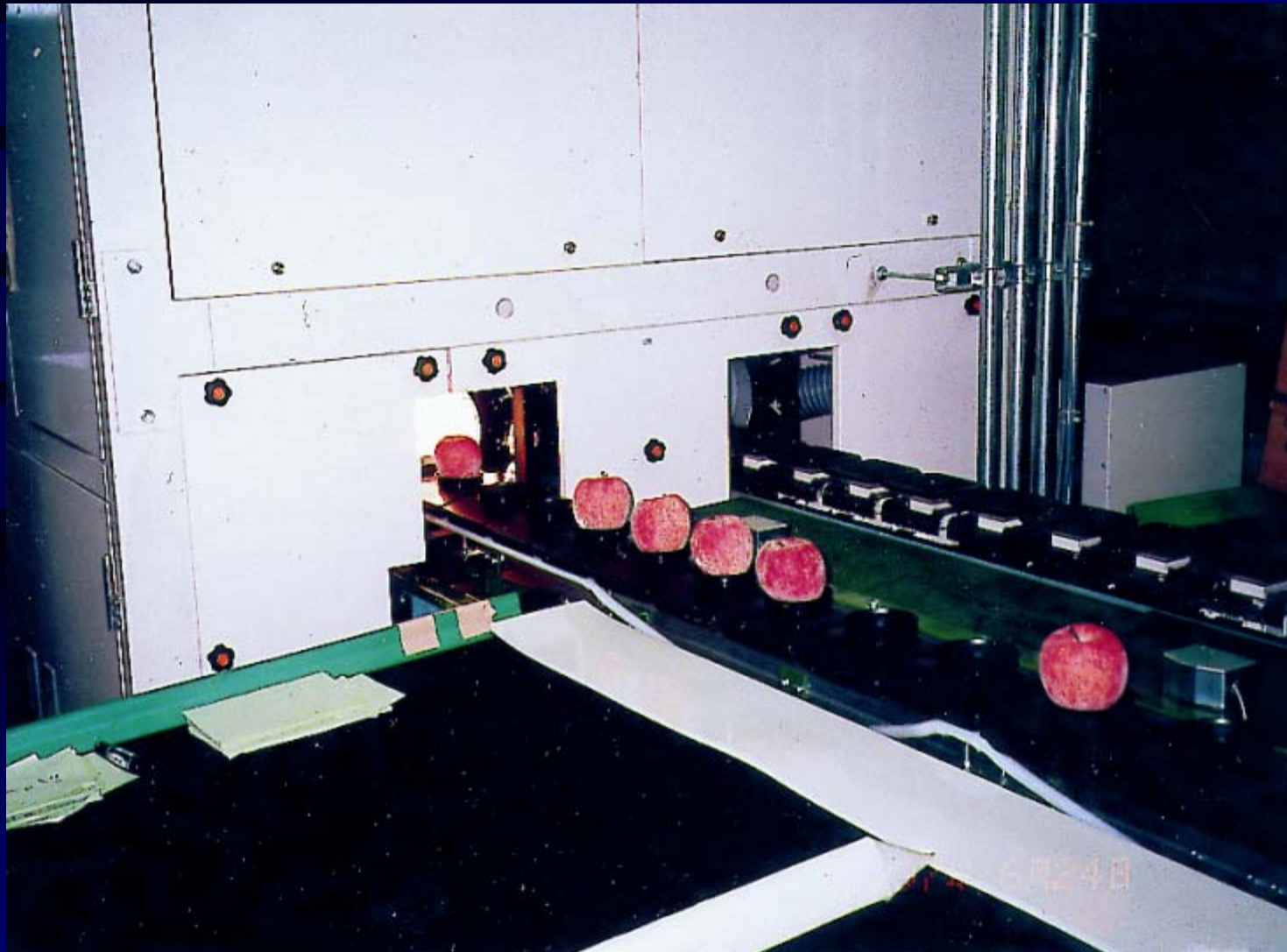


(Level 3)

# Comercial Sorting via NIR



# Comercial sorting via NIR





# Comercial sorting via NIR





# Sorting by internal injuries



# Electronic nose and electronic tongue

- Imitation of sensorial human cells in the nose and on the tongue with bio sensors for sweet, acid, salty and bitter
- Recognition of quality levels in water phase
- Recognition of flavour (chemical compounds) in the gas phase

# Electronic nose, electronic tongue

- Semiconducting metal oxides
- Electrical conducting polymers
- Sensors, which use a mass effect with two groups of vibrational quartz sensors (QMB/QCM sensors) and surface waves sensors (SAW sensors)
- Ion selective electrodes



**Table 2**  
Recent cases of electronic nose application to food quality and safety characterization.

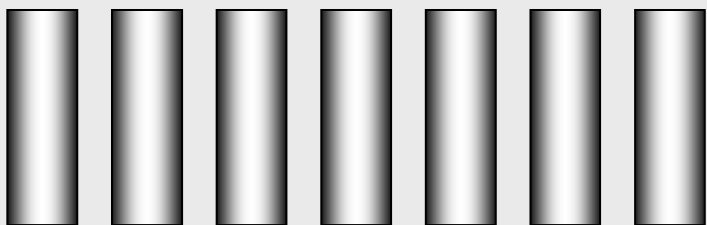
Application case	Aim of use	Researcher(s)
Egg	Monitoring storage time and quality attributes	Yongwei et al. (2009)
Meat	Freshness assessment	Musatov et al. (2010)
	Qualitative and quantitative detection of beef fillets spoilage	Argyri et al. (2010)
	Shelf life prediction and modeling	Limbo et al. (2010)
Hard cheeses	Differentiation based on either age or geographical origin and discrimination based on cheese variety	Gursoy et al. (2009)
Tomato	Assessment of microbial contamination in processed tomatoes	Concina et al. (2009)
	Storage shelf life monitoring	Gomez et al. (2008)
	Monitoring changes of tomato aroma during drying	Pani et al. (2008)
Carrot	Volatile monitoring and control in microwave drying	Li et al. (2009a)
Milk	Identification of different milk flavorings	Wang et al. (2010)
Breast milk	Antioxidant capacity and aroma quality and safety assessment	Li et al. (2009d)
Japanese green tea	Identification of tea types and their particular flavor	Yang et al. (2009)
Wine	Discrimination among types of wine	Lozano et al. (2008)
	Threshold detection of aromatic compounds	Santos et al. (2010)
	Classification according to geographic origin	Cynkar et al. (2010)
Olive oil	Identifying the geographical origin of Liguria extra virgin olive oil	Casale et al. (2010)
	Detection of adulteration with rapeseed and sunflower oils	Mildner-Szkudlarz and Jelen (2010)
Virgin olive oil	Monitoring of oxidative status evolution and sensory analysis of oil with different phenolic content	Lerma-Garcia et al. (2009)
Alcoholic beverage	Off-flavor detection	Ragazzo-Sanchez et al. (2009)
Wine grape	Postharvest dehydration assessment of the grapes	Santonico et al. (2010)
Honey	Geographical origin characterization	Cacic et al. (2009)
Apricot	Monitoring of the storage period	Defilippi et al. (2009)
	Evaluation of quality and breeding perspectives	Gatti et al. (2009)
Sea bass	Freshness decay and shelf life predictive modeling	Limbo et al. (2009)
Pear	Prediction of acidity, soluble solids and firmness	Zhang et al. (2008)
Blueberry	Disease detection and classification	Li et al. (2010a)
Wheat	Analysis of fungal volatile	Perkowski et al. (2008)
	Discrimination of storage age	Pang et al. (2008)
Rice	Differentiation among rice varieties	Zheng et al. (2009)
Chickpea	Recognition among varieties with different milling and physicochemical properties	Ravi and Harte (2009)
Pineapple	Shelf life evaluation of fresh-cut fruit	Torri et al. (2010)
Peach	Characterization of peach cultivars and monitoring ripening stage during shelf life	Benedetti et al. (2008)
	Peach quality attribute evaluation	Zhang and Wang (2009)
Citrus juice	Classification based on fruit type, cultivar and treatment	Reinhard et al. (2008)
Mango fruit	Discrimination of mango fruit maturity	Lebrun et al. (2008)
	Ripeness and rot evaluation	Li et al. (2009c)
Coffee	Discrimination of complex mixtures	Suslick et al. (2010)
	Quality control through the detection of defects in cup tests	Rodriguez et al. (2010)
Fish	Freshness monitoring	Barat et al. (2008)
Virgin coconut oil	Detecting the adulteration	Marina et al. (2010)
Feeding fat	Classification	Van Ruth et al. (2010)
Octopus	Spoiling and formaldehyde-containing characterization	Zhang et al. (2009)
Bread	Aroma monitoring during baking	Ponzoni et al. (2008)
Infant cereals	Evaluation of antioxidant properties and aroma quality	Li et al. (2010b)

**Table 1**  
Some more recent applications of electronic tongue in food quality and safety characterization.

Application case	Aim of use	Researcher(s)
Tomato	Analysis of tomato taste	Beullens et al. (2008)
Wine	Age prediction and organic acids and phenolic compounds quantification	Rudnitskaya et al. (2010)
Beer	Assessment of bitterness intensity and suppression effects	Legin et al. (2009)
	Quantification of real extract, real fermentation degree, alcohol content, pH, bitterness, color, polyphenol and CO <sub>2</sub> content	Polishin et al. (2010)
Mineral water	Classification	Men et al. (2009)
Minced meat	Prediction of NaCl, nitrate and nitrite contents	Labrador et al. (2010)
Tunisian water	Discrimination among samples	Sghaier et al. (2009)
Olive oil	Evaluation of the phenolic content of extra virgin olive oils	Rodriguez-Mendez et al. (2008)
	Characterization with different degree of bitterness	Apetrei et al. (2010)
Tea	Classification of black tea taste	Palit et al. (2009)
	Discrimination of Xihulongjing tea grade	Xiao and Wang (2009)
Milk	Classification of milk originating from various producers	Ciosek and Wroblewski (2008)
	Identification of goat milk adulteration with bovine milk	Dias et al. (2009)
	Adulteration recognition	Paixao and Bertotti (2009)
	Monitoring changes in probiotic fermented milk during storage	Hruskar et al. (2010)
Wine consumed with seafood	Evaluation of effect of sulfur dioxide on formation of fishy off-odor and undesirable taste	Fujita et al. (2010)
Orange juice	Citric acid assessment	Medeiros et al. (2009)
Soybeans	Identification and discrimination of different soybeans cultivars with genetically distinct characteristics	Gregorut et al. (2009)
Non-alcoholic beverage	Evaluation of juice level	Peres et al. (2009)
Water	Study of water quality in fish tank	Chang et al. (2008)
Honey	Classification of honey samples of different floral origins and geographical origins	Wei et al. (2009)
Natural water	Recognition and prediction of common anions chloride, sulfate and bicarbonate	Labrador et al. (2009)
Chinese tea	Correlation with sensory properties and classification according to geographical origin and grade level	He et al. (2009)
Fish	Freshness monitoring	Gil et al. (2008)
Edible oils	Discriminating oils on the basis of their quality and geographical origin	Oliveri et al. (2009)
Chicken carcass	<i>Salmonella typhimurium</i> detection	Lan et al. (2008)
Beverage types	Determining taste-causing compounds	Sun et al. (2008)
	Recognition among the types	Ciosek et al. (2009)
Sport drinks	Evaluation of salt region	Wu et al. (2008)
Green tea	Determination of caffeine content and main catechins contents	Chen et al. (in press)
Soft drink	Semi-quantitative and quantitative analysis for differentiation among the beverage based on fruit juice contents	Dias et al. (in press)

Thank you for your attention

**Laser diodes**

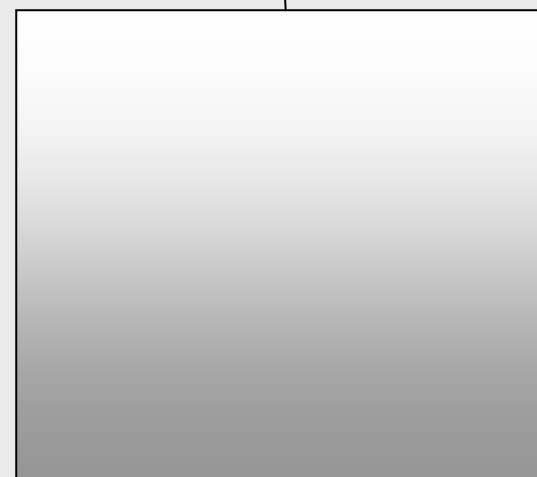
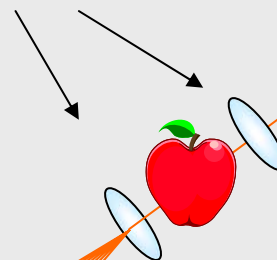


**Laser mirrors**

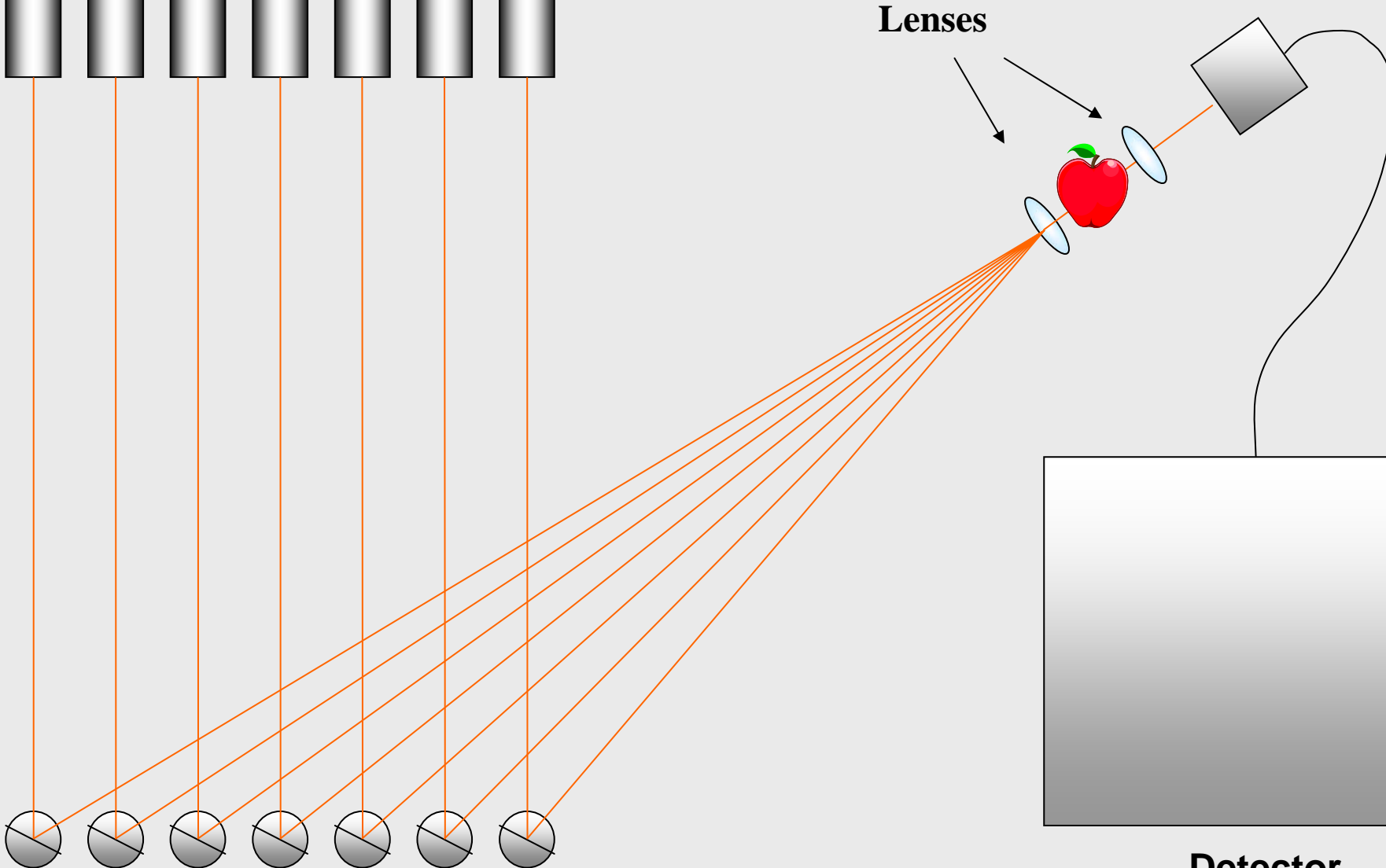


**Receiver**

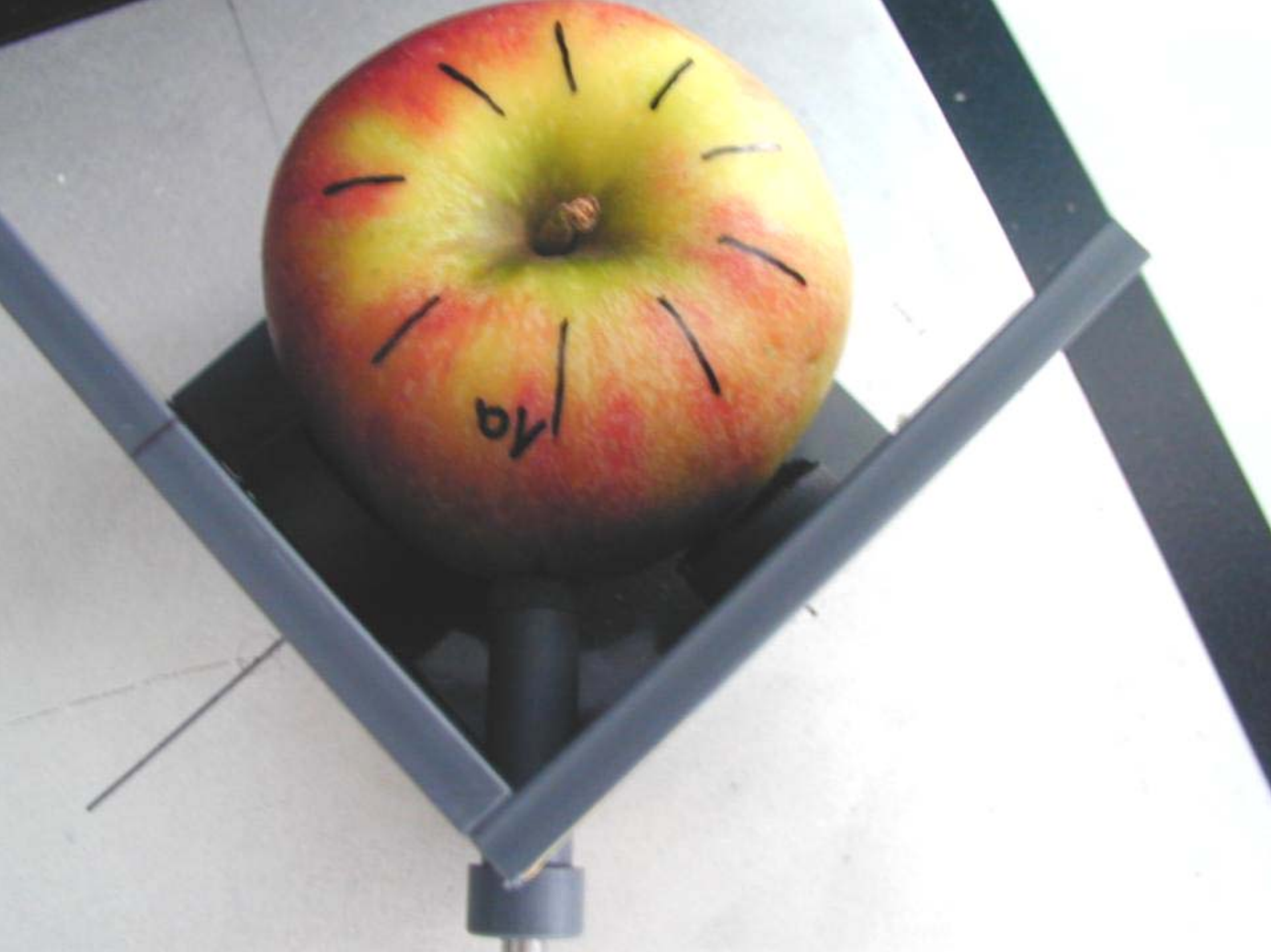
**Lenses**



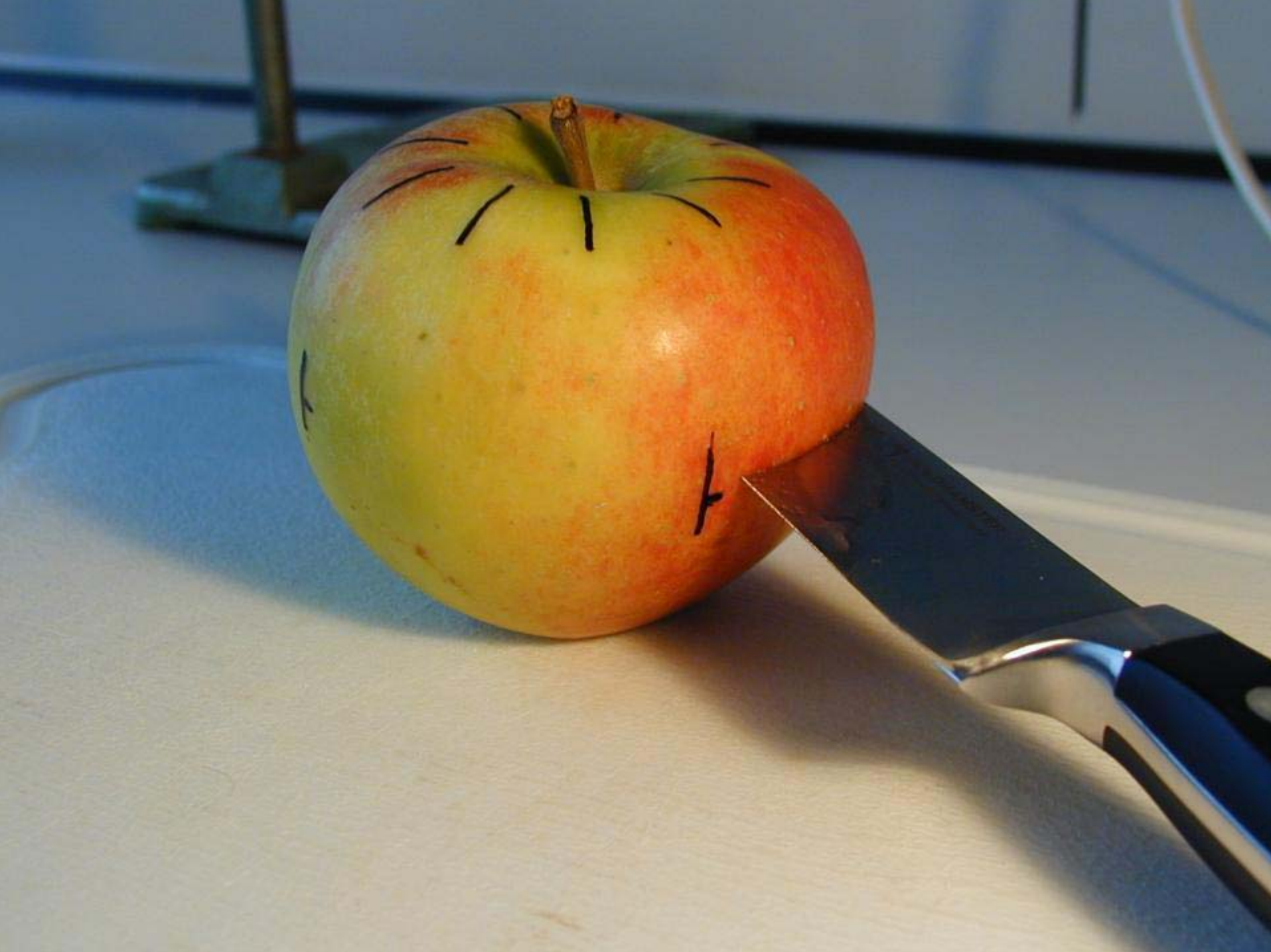
**Detector**

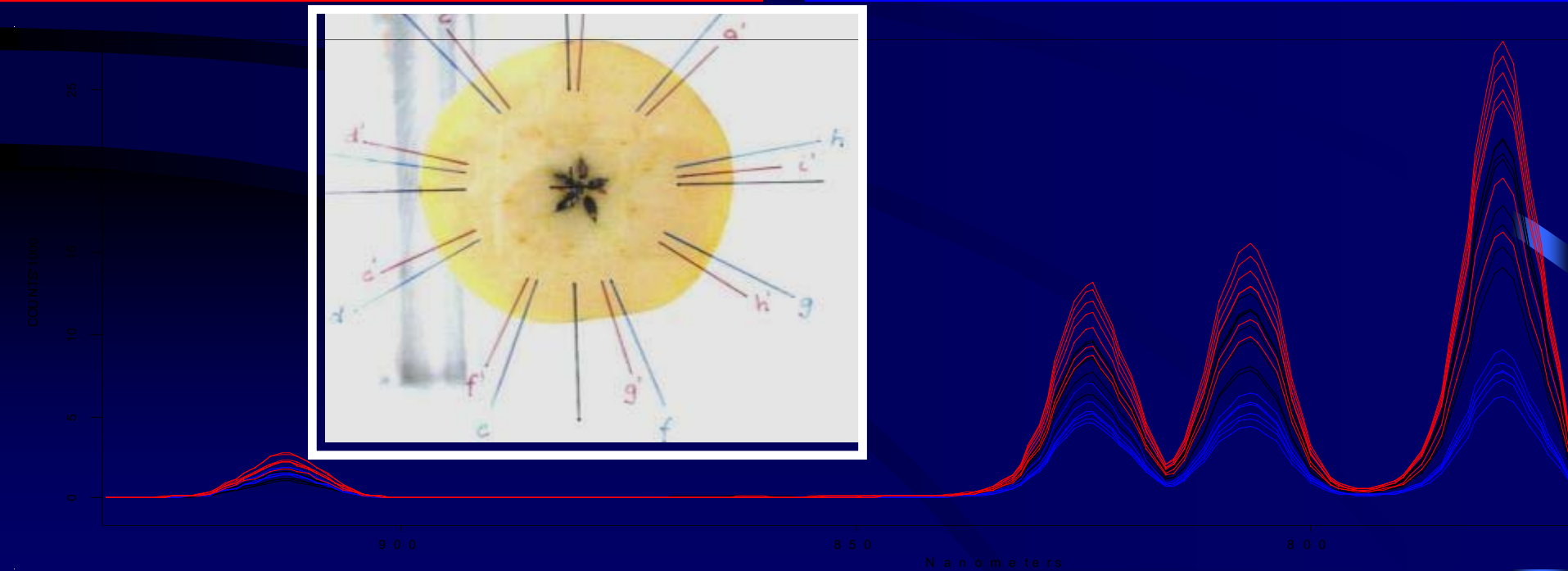
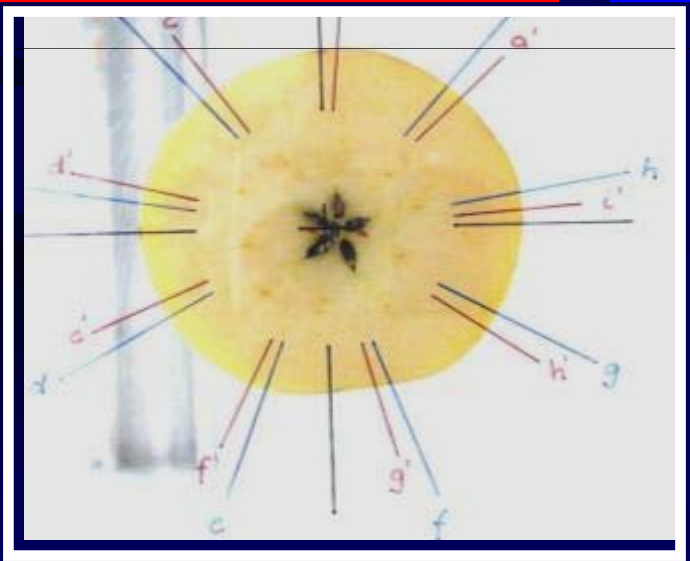
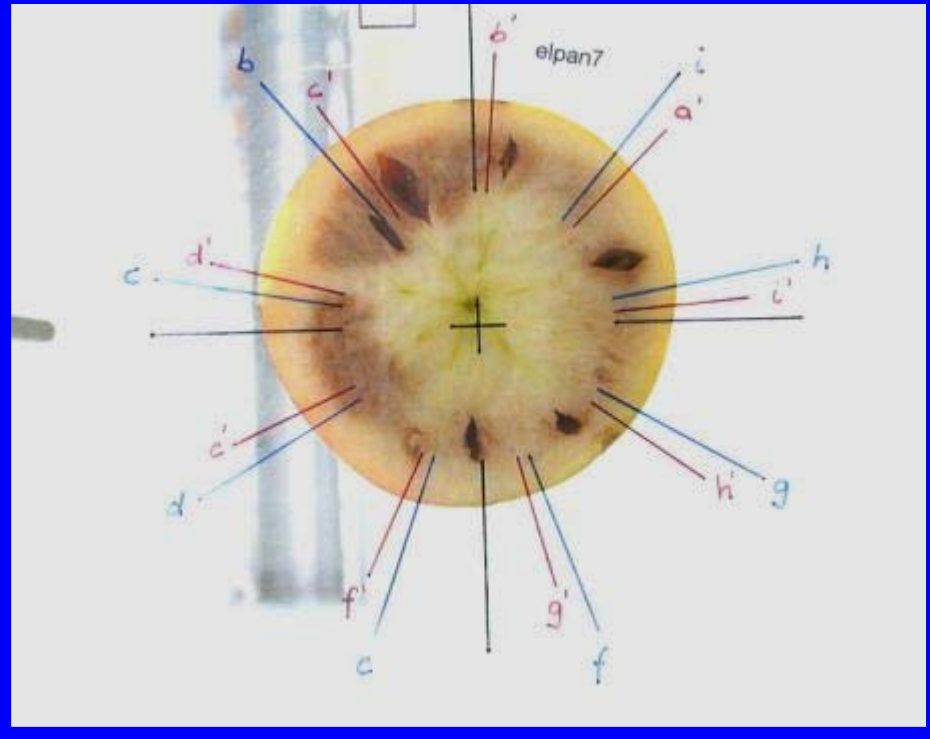
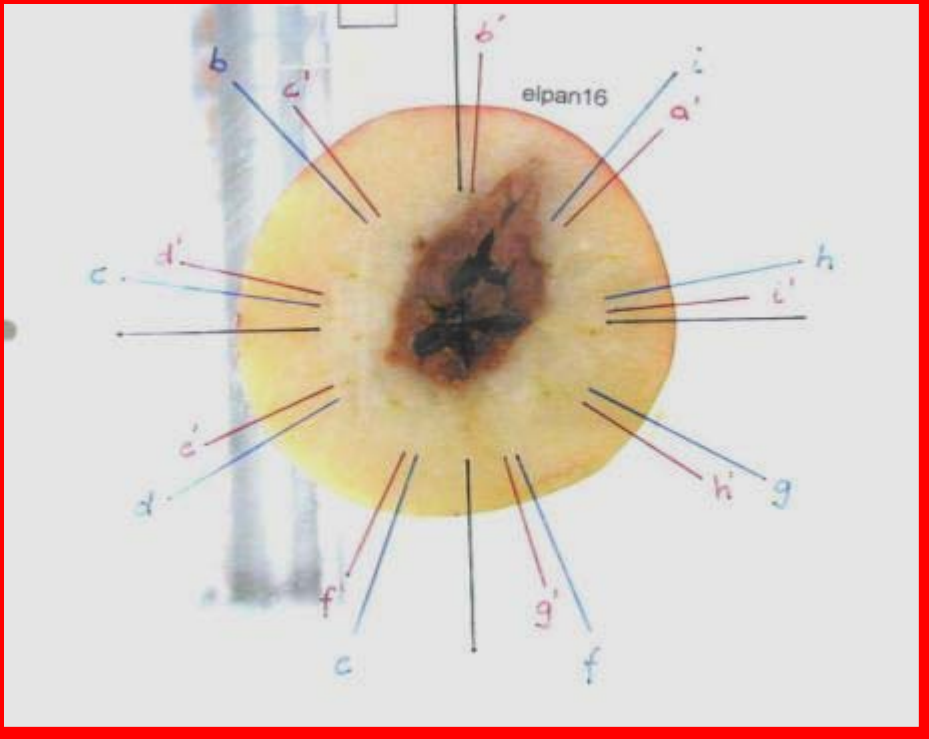




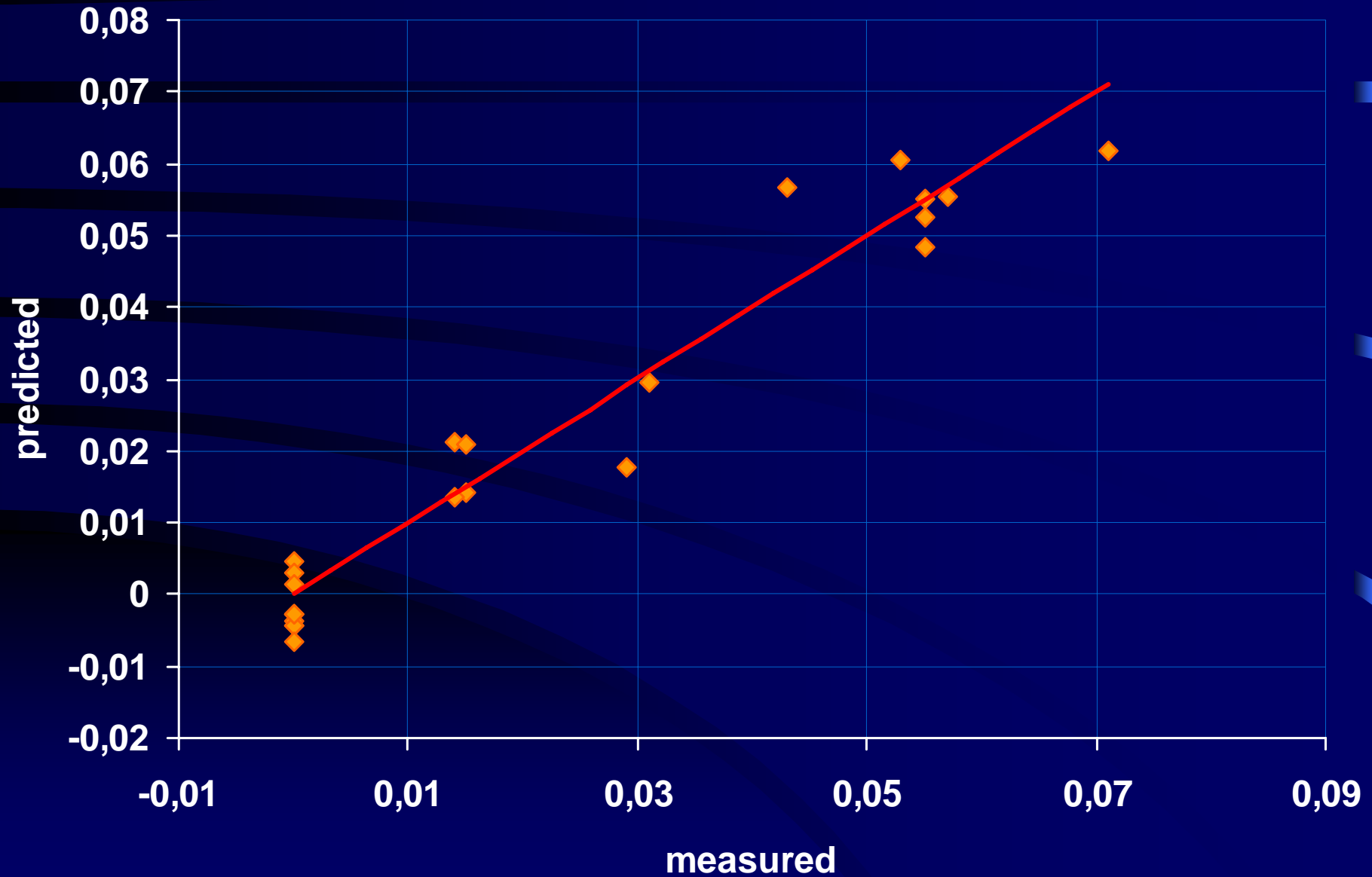






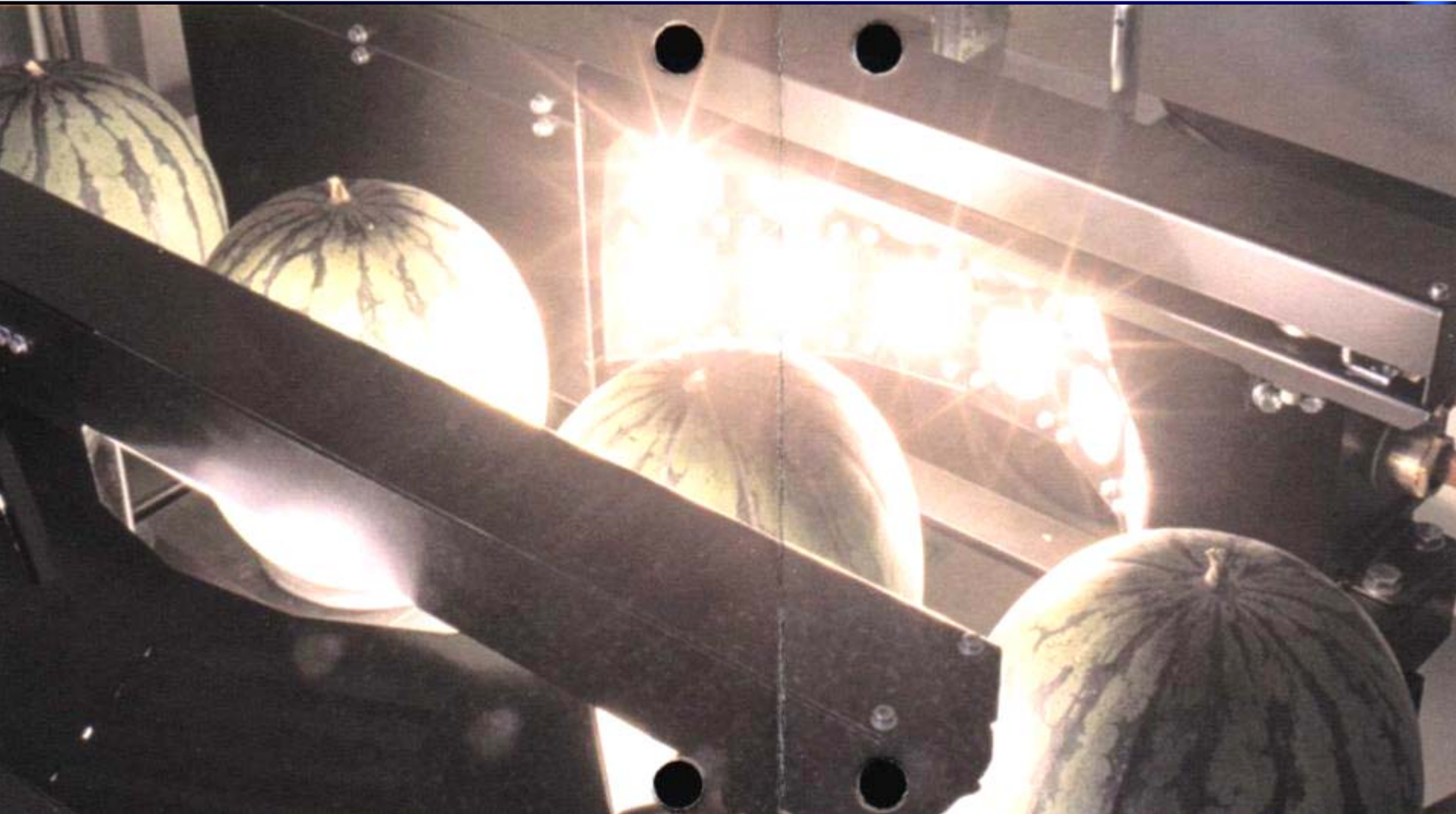


# Internal injuries of apples





# Commercial sorting



# NIR-Miniaturspektrometer – von der Substanzerkennung bis zur nichtinvasiven Blutglucosebestimmung



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## Einleitung

Besonders in der Lebensmittelanalytik spielt die NIR-Spektroskopie schon seit Jahren die wichtige Rolle. Bestenfalls werden können z. B. die Gehalte von Fett, Wasser und Protein. Auch in der Umweltanalytik existieren zahlreiche Anwendungsgebiete, wobei die Vorteile der NIR-Spektroskopie insbesondere in der Feldanalytik zum Tragen kommen.

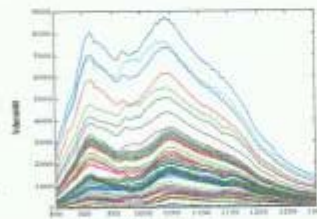
Neue Möglichkeiten ergeben sich ebenso für die Identifizierung von Rohstoffen und Zwischenprodukten in der chemischen und pharmazeutischen Industrie, z. B. in der Wärmegradkontrolle. Die Identifizierung kann unterstützend durch die Ortserkennung, Analysen werden können Pulver, Granulate, Pasten, Gels, Pasten, Flüssigkeiten und Feststoffe mit hoher Zuverlässigkeit.

Die molekularen Anwendungen der NIR-Spektroskopie greifen sich in wesentlichen darauf, daß die elektromagnetische Strahlung in diesem Wellenlängenbereich relativ große Eindringtiefen in das Körpergewebe aufweist ("therapeutisches" bzw. "optisches Fenster"). Vorteile der NIR-Spektroskopie gegenüber räumlichen Verfahren sind, die sie nicht-invasiv, nicht-invasiv, die On-line-Messungen ermöglichen, und die Tatsache, daß in der Regel nur eine einfache Probenzubereitung notwendig ist oder diese gänzlich entfällt.

Da NIR-Spektrometer leicht zu miniaturisieren sind, lassen sich portable, wenn nötig batteriebetrieben, Messgeräte realisieren. Allerdings erfordert die Antwortung nicht-invasiver chemischer Methoden, wie Partial Least-Squares Regression (PLS) und künstliche neuronale Netze (ANN). Die Entwicklung solcher Messsysteme wurde daher nicht zuletzt durch die Vorhandenheit von preiswerten Miniaturrechnern ermöglicht, die mit dem Spektrometer gekoppelt als korrelierte Regressur- und Auswerteinheiten dienen können. Durch die Kopplung der Spektrometer mit faseroptischen Modulen kann die räumliche Trennung von Probe und Messgerät gewährleistet werden.

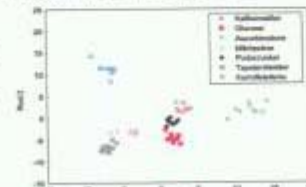
## Identitätsprüfung

Mit dem NIR-Miniaturspektrometer soll die Identität von sieben verschiedenen pulverförmigen Substanzen (Kaffeebohnen, Glucose, Ascorbinsäure, Milchpulver, Puderzucker, Tapiokastärke und Kartoffelstärke) geprüft werden, die visuell schlecht zu unterscheiden sind. Hierzu wurden von jeder Substanz je sechs Messungen jeweils drei Spektren im Wellenlängenbereich 850 – 1300 nm aufgenommen.



NIR-Spektren der pulverförmigen Substanzen.

Die Auswertung der Spektren wurde mit einer Linearen Diskriminanzanalyse (LDA) durchgeführt. Die Spektren der Substanzen 1 ... 3 dienen als Lernkennwerte und die der Substanzen 4 ... 6 als Testkennwerte. Die Verwendung eines Testkennwertes ist zur Validierung des Klassifikationsmodells erforderlich.



Repräsentation der Substanzen auf der Fläche, die durch die ersten beiden Diskriminanzfunktionen aufgespannt wird.

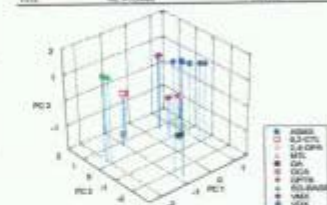
Wie die Klassifikationsresultate zeigen, wurden alle Spektren der Testkennwerte den jeweils korrekten Klassen zugeordnet.

Substanz	Kaffeebohnen	Glucose	Ascorbinsäure	Milchpulver	Puderzucker	Tapiokastärke	Kartoffelstärke
Lernkennwerte	10	10	10	10	10	10	10
Testkennwerte	10	10	10	10	10	10	10
Klassifizierung	10	10	10	10	10	10	10
Genauigkeit	100%	100%	100%	100%	100%	100%	100%

Zur Identifizierung der Ausgangsprodukte in einem chemischen Reaktor soll ebenfalls die NIR-Spektroskopie herangezogen werden. Zu unterscheiden sind zehn bei Raumtemperatur flüssige Verbindungen (s. Tabelle).

Substanz	Verbindung	Farbe
AcOH	Aceton	farlos
EA	Diäthyläther	farlos
EA	Diäthyläther	farlos
EA	Diäthyläther	farlos
EA	Diäthyläther	farlos
EA	Diäthyläther	farlos
EA	Diäthyläther	farlos
EA	Diäthyläther	farlos
EA	Diäthyläther	farlos
EA	Diäthyläther	farlos

Gemessen wurde in drei Messungen, die eine durch ein Lernkennwert. Die Auswertung der Spektren erfolgte hierbei über eine Hauptkomponentenanalyse (PCA), wobei die Zugehörigkeit der Testspektren über die Korrelation als relatives Ähnlichkeitsmaß ermittelt wurde.

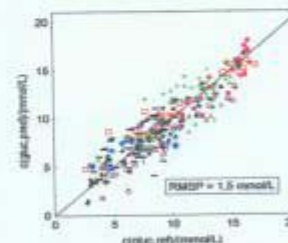


Darstellung der ersten drei Hauptkomponenten des Lernkennwertes.

## Nichtinvasive Blutglucosebestimmung

Mithilfe NIR-Spektroskopie soll die Konzentration der Blutzucker (des Blutzucker) nicht-invasiv bestimmt werden. Hierzu werden im Spektralbereich 850 – 1300 nm Spektren von verschiedenen Proben bei variierenden Blutzuckerkonzentrationen aufgenommen. Kalibrierung wurde mittels einer Partial Least-Squares Regression (PLS) und künstlichen neuronalen Netzen (ANN).

Für Ein-Personen-Experimente wurden zum Teil sehr gute Ergebnisse erzielt, die sich grundsätzlich nicht auf Mehr-Personen-Experimente übertragen ließen. Deshalb fanden Verfahren zur Spektroskopischen Anwendung, mit denen sehr viele Spektren akkumuliert werden können.



Wiederfindungsplot eines personalisierten kalibrierten Kalibrierungsmodells, das mit einem künstlichen neuronalen Netz erstellt wurde. Der Datensatz wurde vor der Kalibrierung einem sequentiellen Selektionsalgorithmus unterworfen.

## Zusammenfassung

Miniatüre NIR-Spektroskopie können Probleme der Identifizierung, z. B. für die Wärmegradkontrolle, und Konzentrationsbestimmungen, z. B. der Blutzucker, gelöst werden. Allerdings müssen hierzu fortgeschrittene chemische Methoden wie die Hauptkomponentenanalyse, die Diskriminanzanalyse, die Partial Least-Squares Regression und die künstlichen neuronalen Netze herangezogen werden. Hierbei ist es durch Miniaturisierungen möglich, kleine batteriebetriebene Geräte zu verwenden, mit denen besonders vorteilhaft Probe- und Feldanalysen durchgeführt werden können, die aber auch in der klinischen Analytik für Selbstmessungen durch die Patienten geeignet sind.

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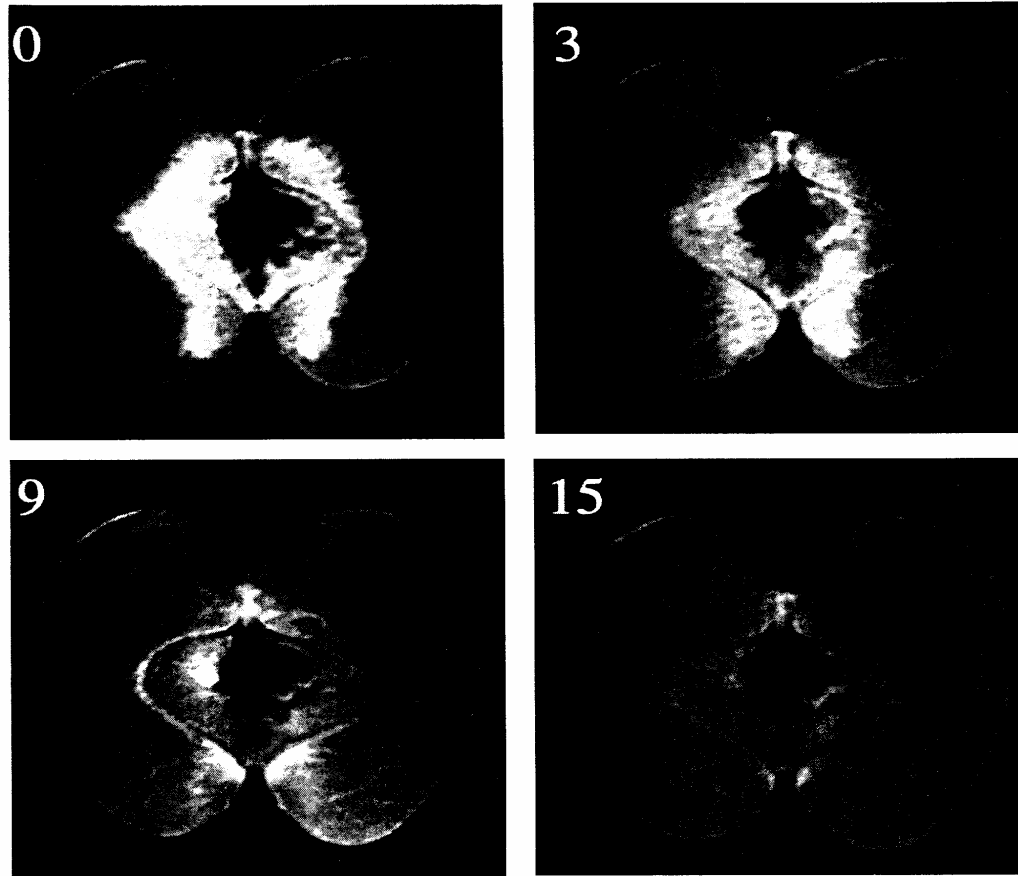


Fig. 3. Watercore amelioration in apple (cv. Fuji) during 20 weeks cold storage at 0°C. Proton-density weighted images ( $T_E = 40$  ms;  $T_R = 1$  s) are of a longitudinal equatorial slice of a Fuji apple imaged on successive occasions during the storage period. Numbers indicate weeks in storage. Pixel sizes are  $0.39 \times 0.39$  mm with a 5 mm slice thickness (Clark et al., 1996).