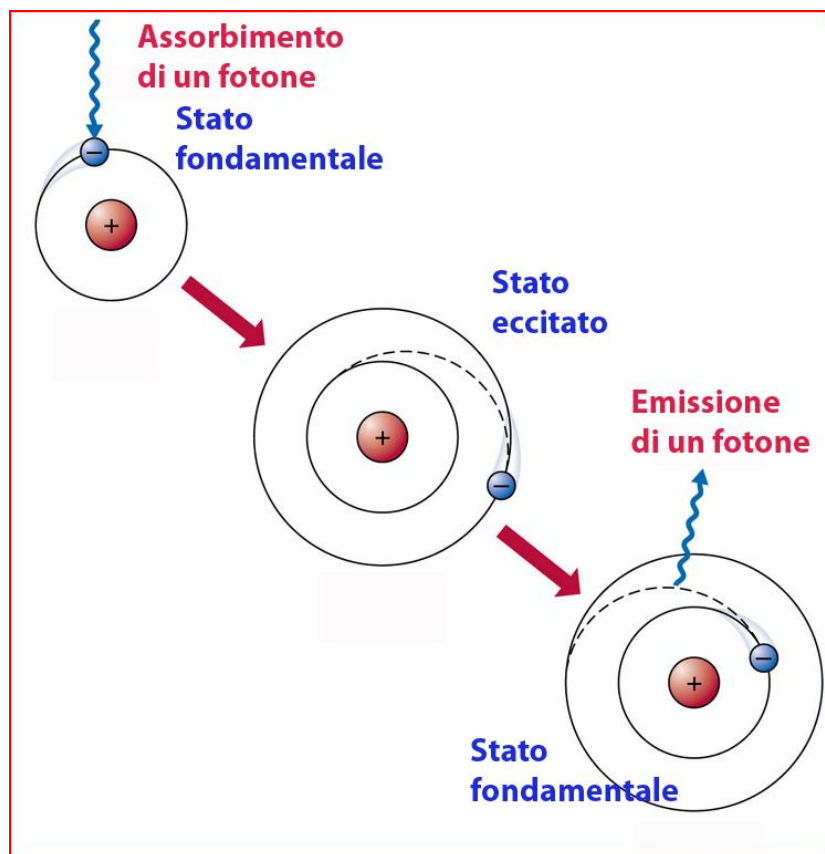
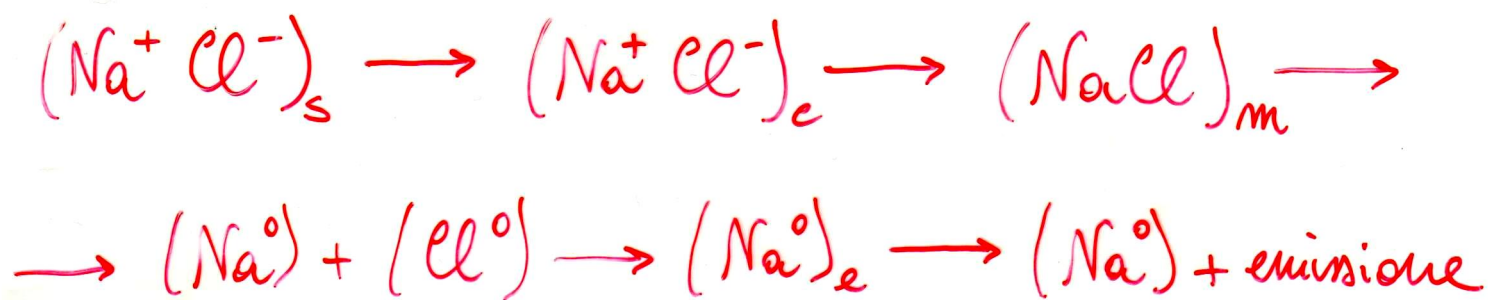


SAGGI ALLA FIAMMA

colorazioni

catione	caratt. fiamma	col.dominante	λ (nm)	altre coloraz.
LITIO	intensa	ROSSO CARMINIO	671	
SODIO	intensa	GIALLO	589	
POTASSIO		VIOLA PALLIDO	768	rosso (vetro al Co)
CALCIO	intensa, fugace	ARANCIONE	629	verde
STRONZIO		ROSSO VIVO	673	arancio, azzurro
BARIO	persistente	VERDE PALLIDO	493	arancio
RAME	vivace, fugace	VERDE-TURCHESE	325	



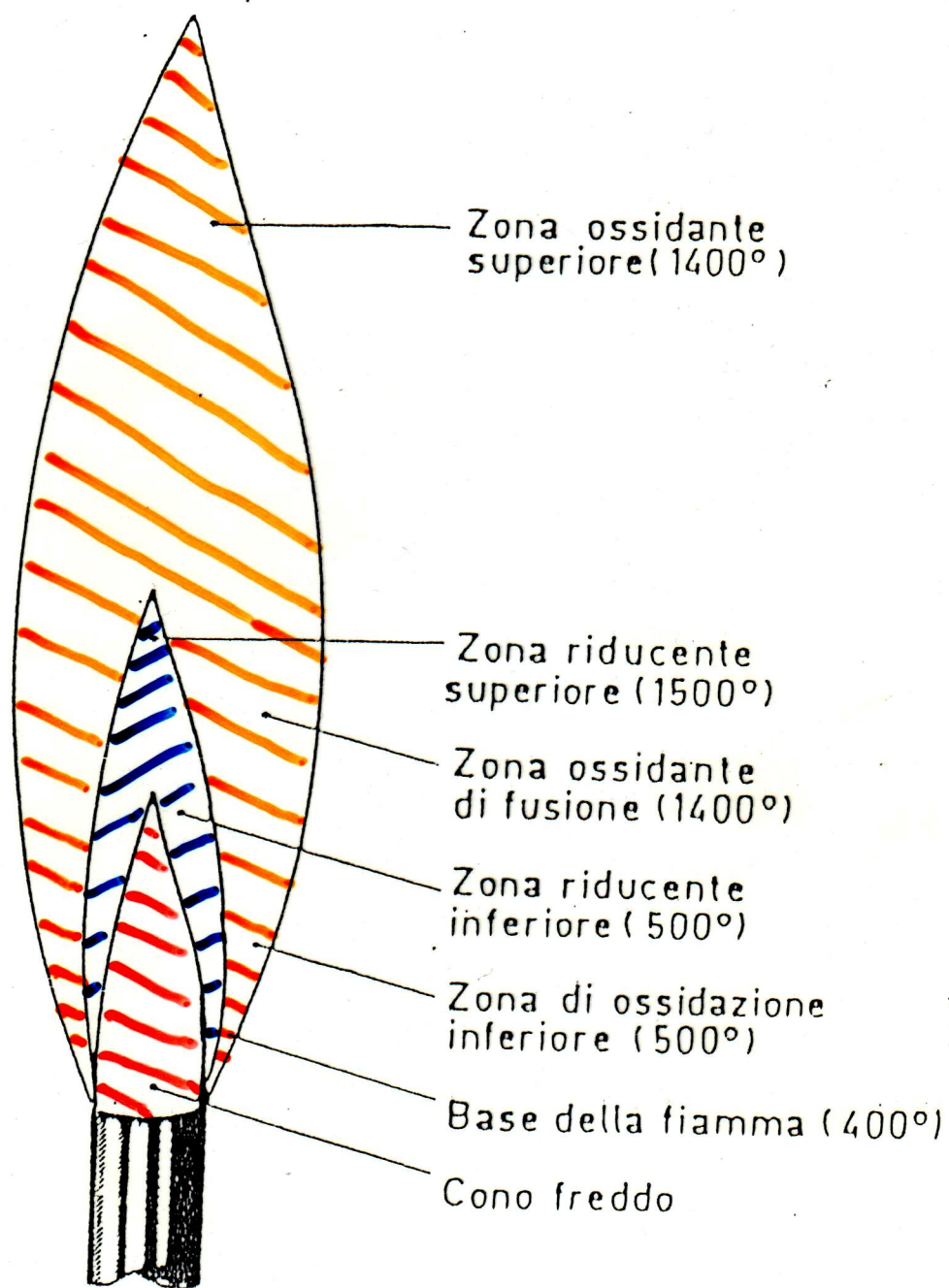
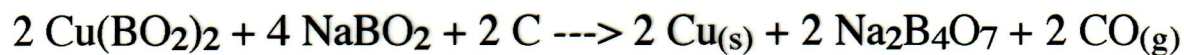
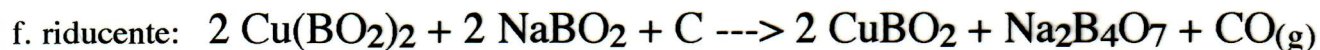
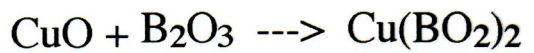
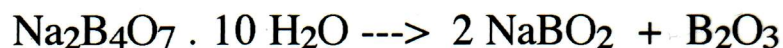


Fig. 4.2.1. - Le zone della fiamma.

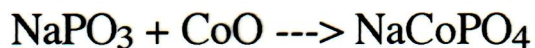
SAGGI ALLA PERLA



colorazioni

catione	f oss. - caldo	f oss. - freddo	f rid. - caldo	f rid. - freddo
COBALTO	rosa	azzurra	rosa	azzurra
FERRO	gialla	incol. o gialla	verde	verde bottiglia
CROMO	giallo scura	verde smer.	verde	verde smer.
MANGANESE	rosa	rosa	incolore	incolore
NICHEL	rosso bruna	giallo bruna	grigia	grigia
RAME	verde	azzurra	incolore	rosso opaco

Perla alternativa: $\text{Na(NH}_4\text{)HPO}_4 \cdot 4 \text{H}_2\text{O}$



SAGGI AL TUBICINO

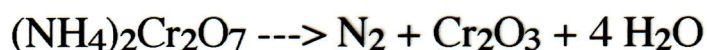
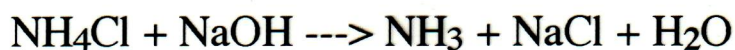
I] Variazione di colore (ossidi termocromici):

<u>ossido</u>	<u>colore a 25°C</u>	<u>colore a >25°C</u>
ZnO*	BIANCO	GIALLO INTENSO
TiO ₂	BIANCO	GIALLO PALLIDO
PbO	GIALLO	ROSSO CUPO (+ fusione)
Bi ₂ O ₃ *	GIALLO	ARANCIO (+ fusione)
Fe ₂ O ₃	ROSSO	NERO
Cr ₂ O ₃	VERDE	GRIGIO
HgO*	ROSSO	NERO (+ decomposizione)

*Importante in F.U.

II] Comparsa di sublimati:

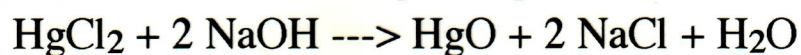
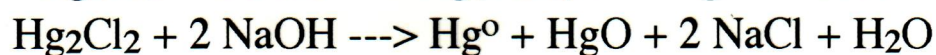
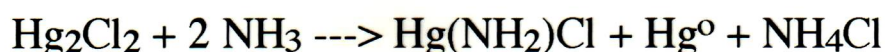
BIANCHI: a) tutti i sali di NH_4^+ + H_2O = solubili
+ OH^- = non cambiano colore



b) tutti i sali di As + H_2O = insolubili (sviluppo di As_2O_3)
+ OH^- = non cambiano colore

c) Hg_2Cl_2 - HgCl_2 + H_2O = solubili
+ OH^- = cambiano colore

(Hg_2^{2+} da BIANCO a NERO per separazione di Hg^0 , Hg^{2+} da BIANCO a GIALLO per formazione di HgO)



II] Comparsa di sublimati:

COLORATI (saggi con Tiosolfato di Sodio):



<u>solfuro</u>	<u>colore</u>
Sb_2S_3	ROSSO MATTONE
As_2S_3	GIALLO
HgS	NERO
S^0	GIALLO OCRA

III] Sviluppo di vapori colorati:

Br^- , I^- e NO_3^- con 1-2 gocce di H_2SO_4 conc. a caldo si ossidano svolgendo vapori colorati:

$\text{Br}^- \longrightarrow \text{Br}_2$	vapori GIALLO-ROSSASTRI di odore sgradevole caratteristico + cartina alla fluoresceina = coloraz. ROSA per formazione di tetrabromofluoresceina
$\text{I}^- \longrightarrow \text{I}_2$	vapori VIOLETTI
$\text{NO}_3^- \longrightarrow \text{NO}_2$	vapori GIALLO-ROSSASTRI di odore sgradevolissimo + cartina alla fluoresceina = nessuna colorazione



Fluoresceina

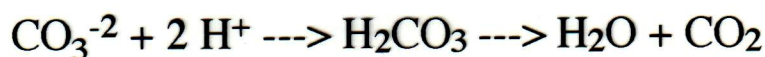
SAGGI DI RICONOSCIMENTO PARTICOLARI

Riconoscimento anione BORATO BO_3^{-3} :

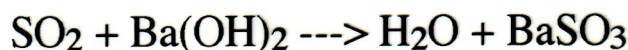


il borato di metile che si forma impartisce alla fiamma del bunsen una colorazione
VERDE

Riconoscimento anione CARBONATO CO_3^{-2} :

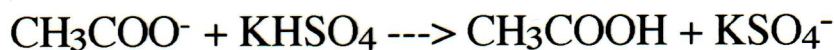


insolubile in H_2O ; solubile in HCl



insolubile in H_2O ; insolubile in HCl

Riconoscimento anione ACETATO CH_3COO^- :

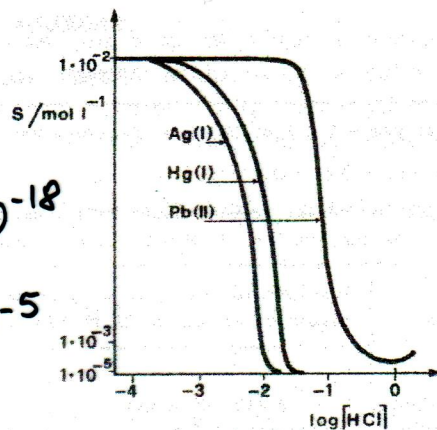
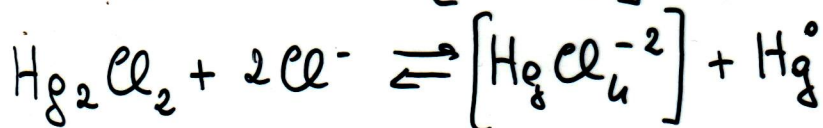
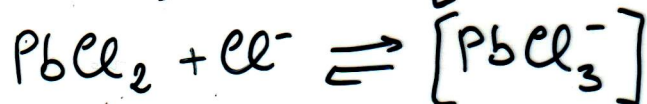
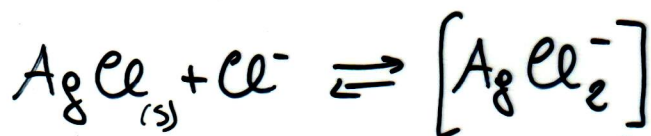
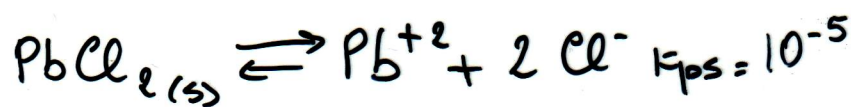
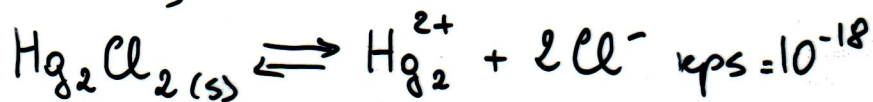
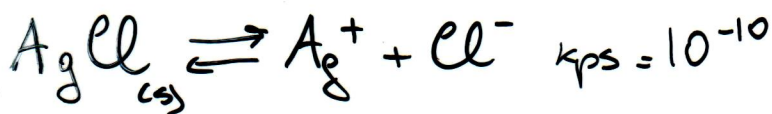


Riconoscimento catione AMMONIO NH_4^+ :



ANALISI DEI CATIONI PER VIA UMIDA (sistemica classica)

1° GRUPPO



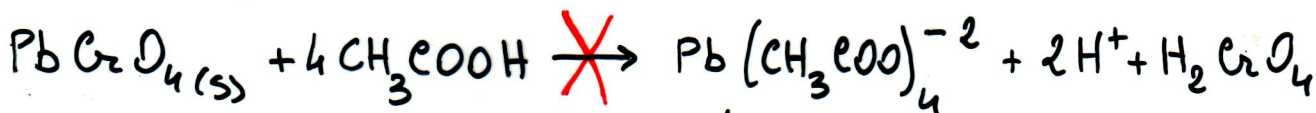
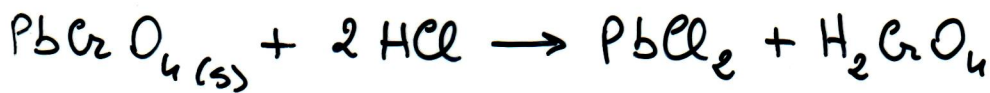
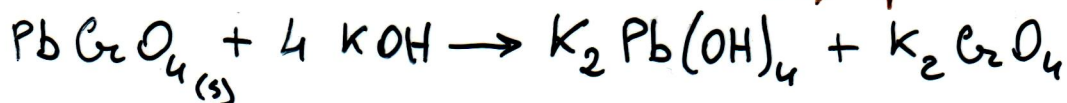
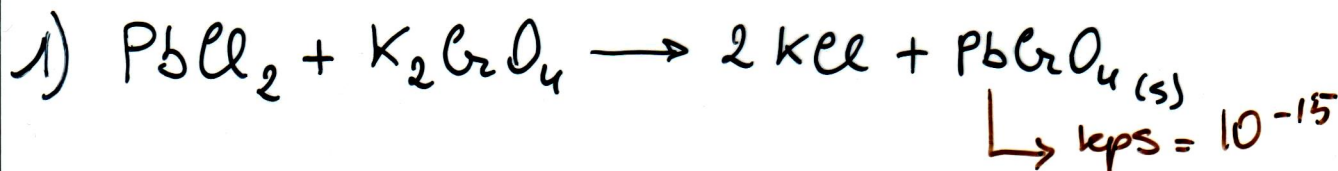
Il primo gruppo:
Ag(I), Hg(I), Pb(II)

Precipitazione dei cationi del primo gruppo in funzione della quantità (mol l⁻¹) di HCl introdotto in soluzioni contenenti inizialmente 1x10⁻² mol l⁻¹ Ag⁺, Hg₂²⁺ o Pb²⁺.

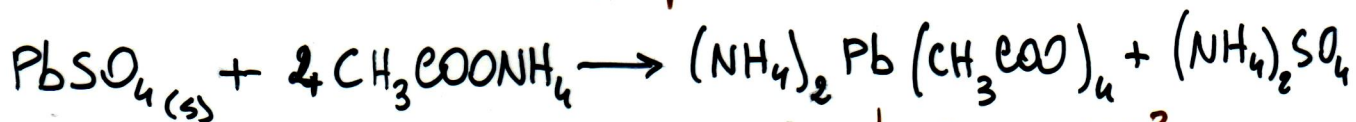
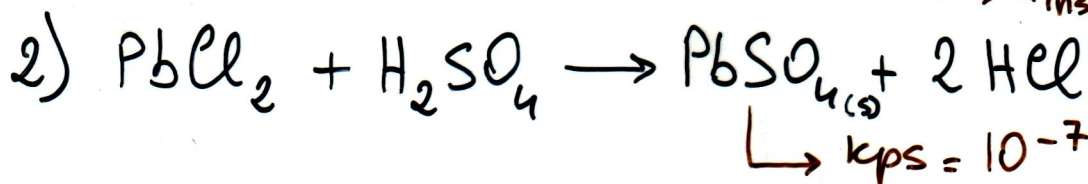
PIOMBO

▷ PbCl₂ in acqua fredda = 8 mg / ml

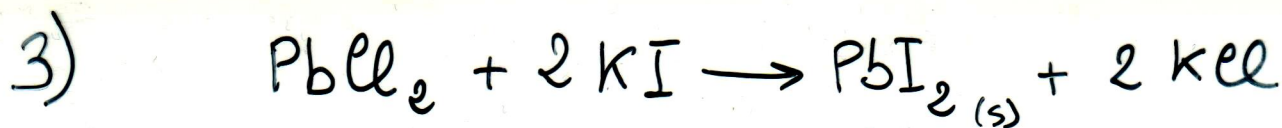
▷ PbCl₂ in acqua calda = 35 mg / ml



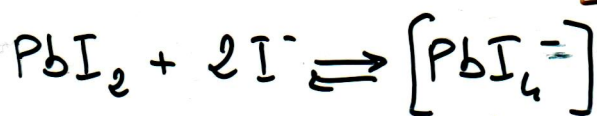
↳ $K_{inst.} = 10^{-3}$



↳ $K_{inst} = 10^{-3}$

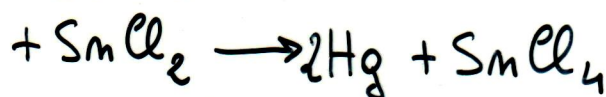


$$\rightarrow K_{ps} = 10^{-8}$$

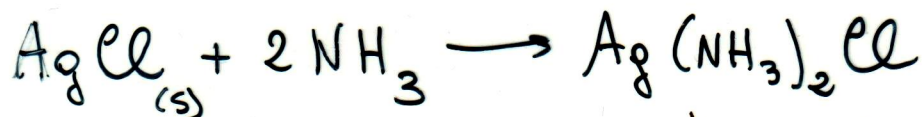


$$\rightarrow K_{inst} = 10^{-5}$$

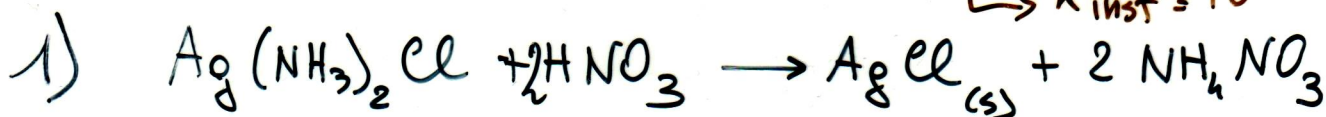
MERCURIO



ARGENTO



$$\rightarrow K_{inst} = 10^{-7}$$



$$\rightarrow K_{ps} = 10^{-16}$$

ATTIVITÀ FARMACOLOGICA E TOSSICOLOGICA

PIOMBO = composti di interesse farmac.: $\text{Pb}(\text{CH}_3\text{COO})_2$
intossicat. cronica: SATURNISMO

interat. gruppi SH proteine (NH_2 , COOH)

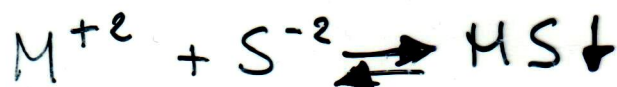
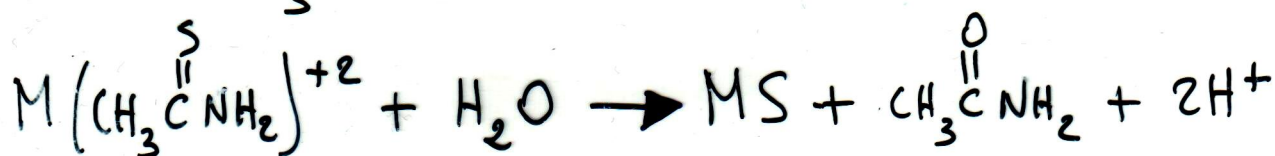
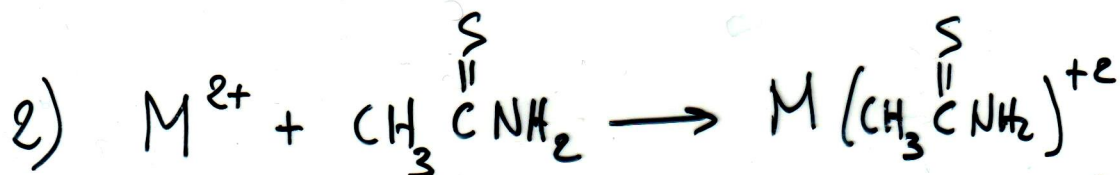
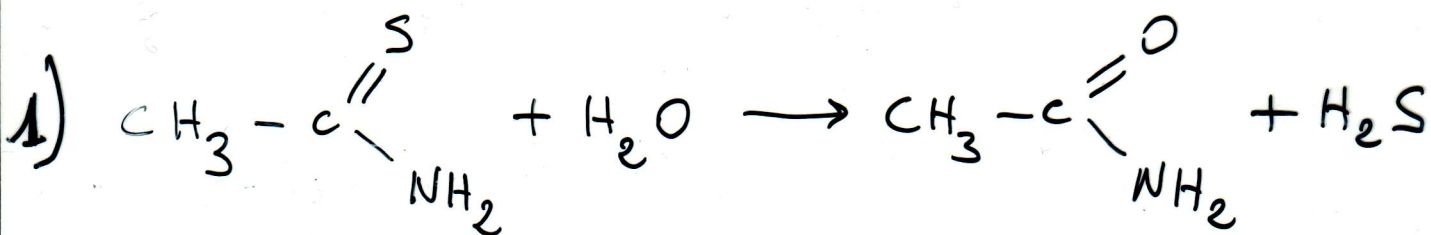
competizione con Ca^{+2} nelle ossa e nei denti

$\text{Pb}(\text{CH}_3\text{COO})_2$ cancerogeno e teratogeno

$\text{Pb}(\text{CH}_2\text{CH}_3)_4$, $\text{Pb}(\text{CH}_3)_4$ = antidebonanti per benzine

$\rightarrow \text{PbCl}_2$, PbSO_3 , PbO , PbBr_2 tossici

2° GRUPPO



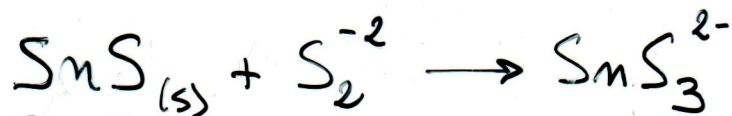
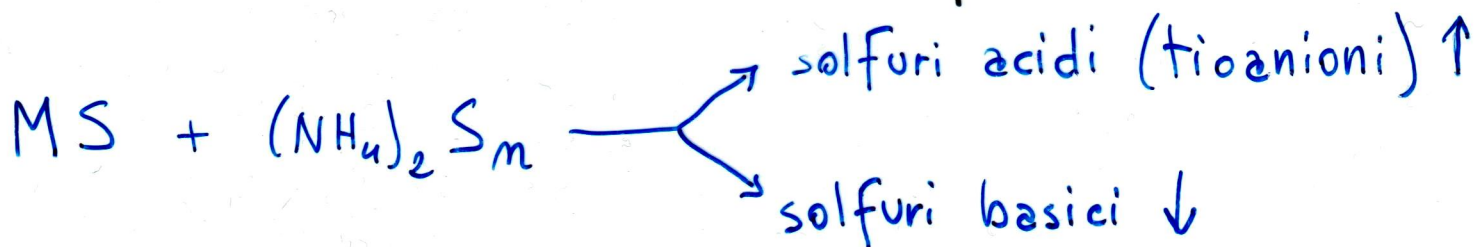
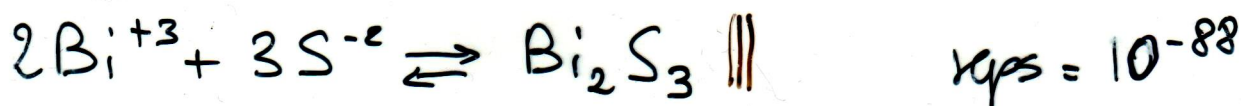
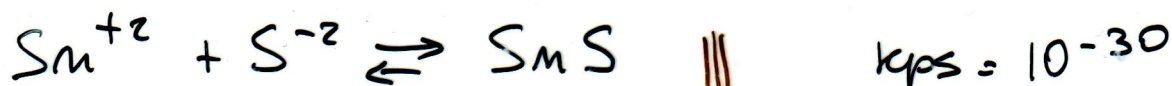
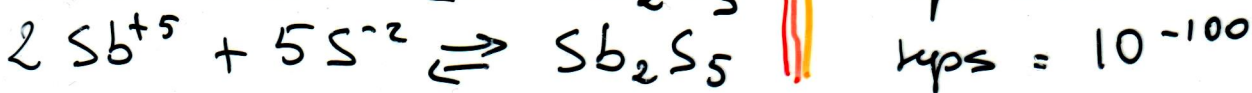
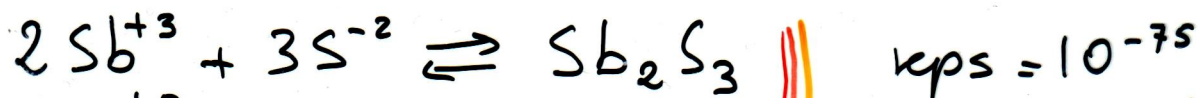
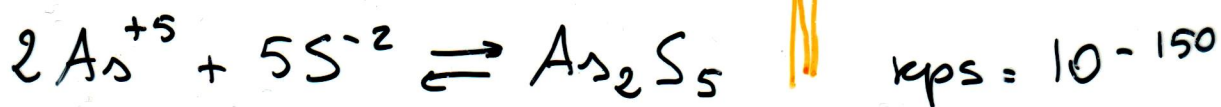
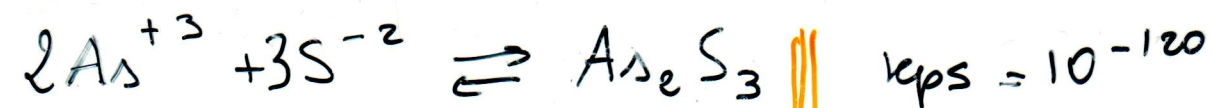
$$K_{a1} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 10^{-7} ; \frac{[\text{HS}^-]}{[\text{H}_2\text{S}]} = \frac{K_{a1}}{[\text{H}^+]}$$

$$K_{a2} = \frac{[\text{H}^+][\text{S}^{=}] }{[\text{HS}^-]} = 10^{-13} ; \frac{[\text{S}^{=}]}{[\text{HS}^-]} = \frac{K_{a2}}{[\text{H}^+]}$$

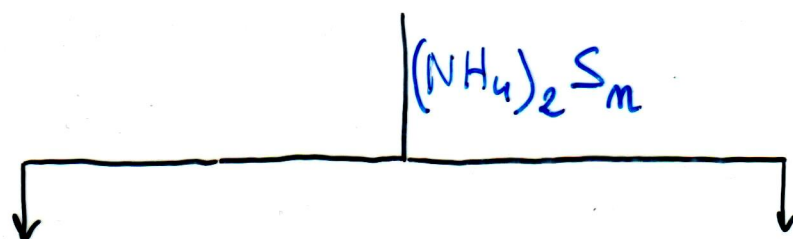
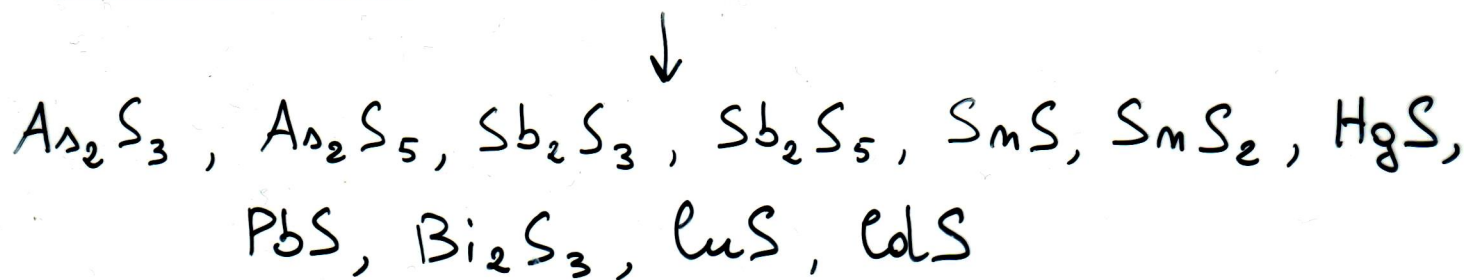
$$K_{a1,2} = \frac{[\text{H}^+]^2 [\text{S}^{=}]}{[\text{H}_2\text{S}]} = 10^{-20} ; [\text{S}^{=}] = \frac{K_{a1,2} \cdot [\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

$$\text{a } \text{pH} = 0 \quad ([\text{H}^+] = 1\text{M}) \quad [\text{S}^{=}] = \frac{10^{-20} \cdot 0,1}{1} = 10^{-21}\text{M}$$

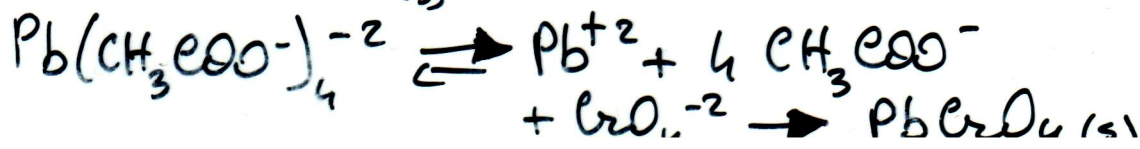
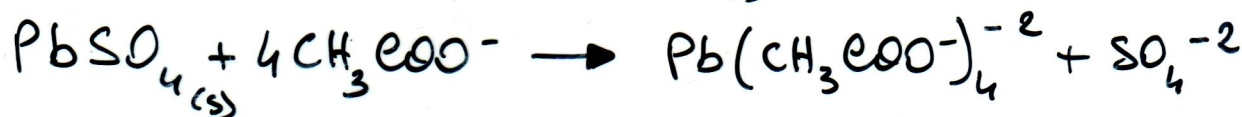
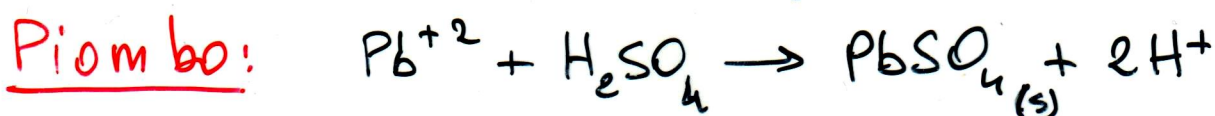
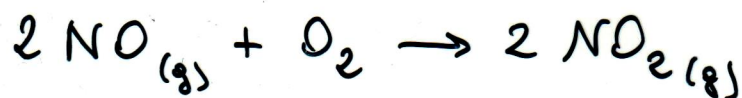
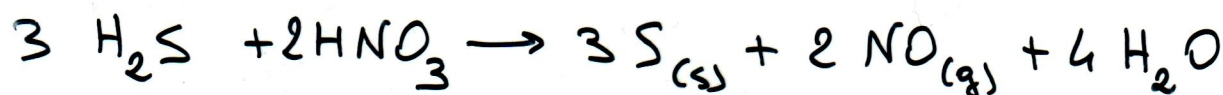
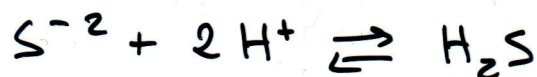
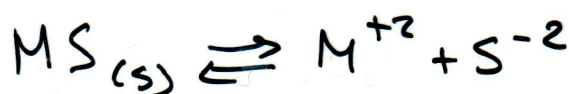
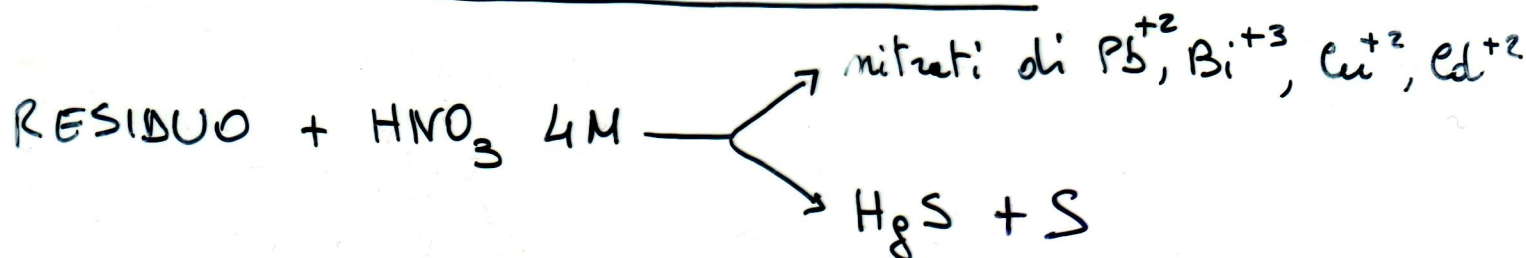




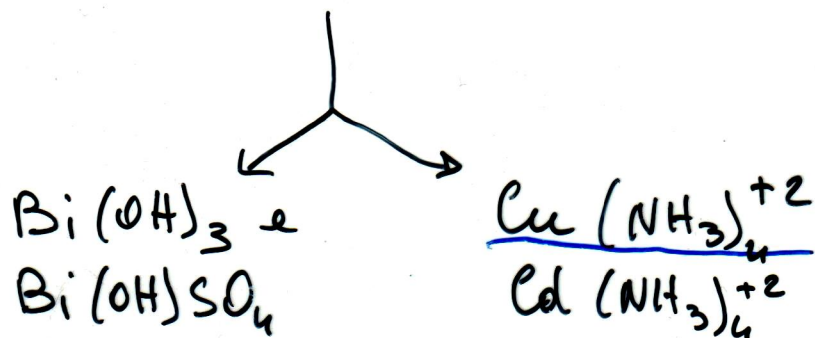
2° GRUPPO - H_2S a TIOACETAMMIDE pH 0 - 2.2



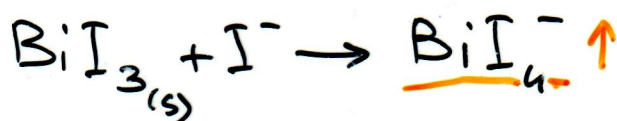
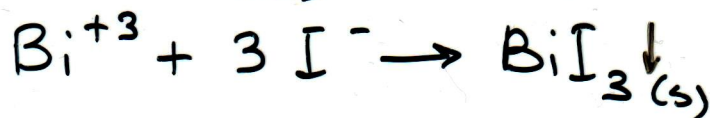
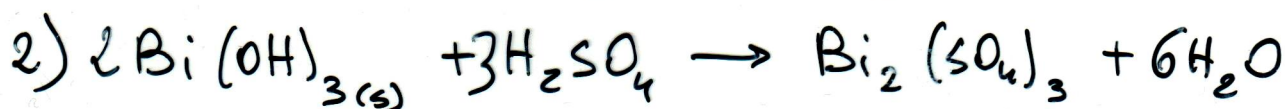
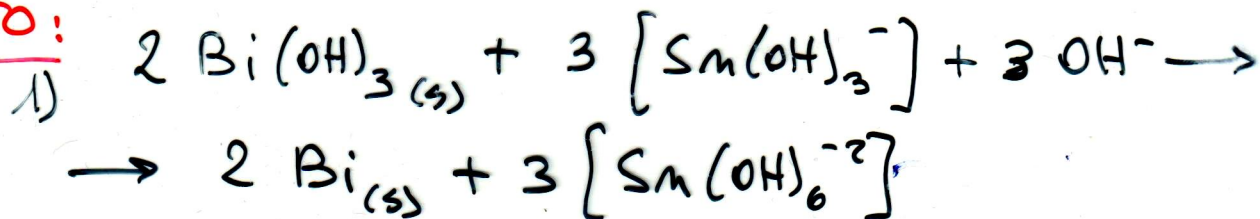
1° SOTTOGRUPPO



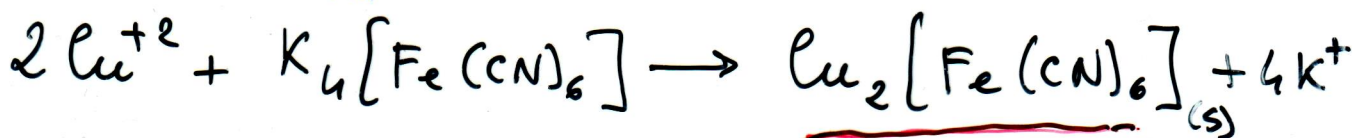
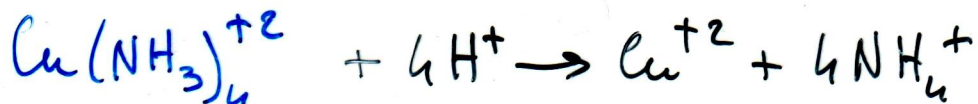
soluzione con
solfati di Bi^{+3} , Cu^{+2} , Cd^{+2} + NH_3 6 M



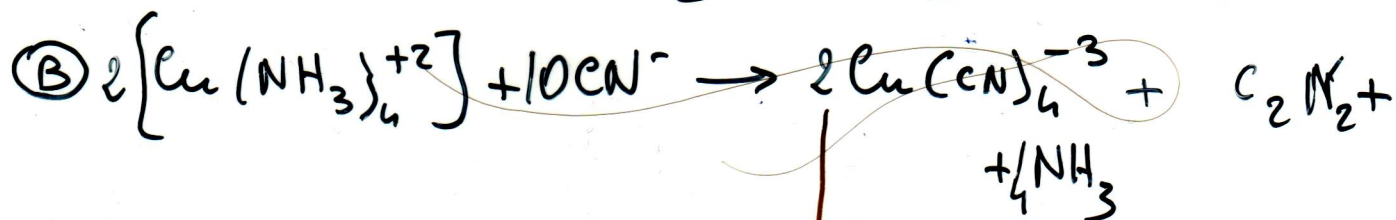
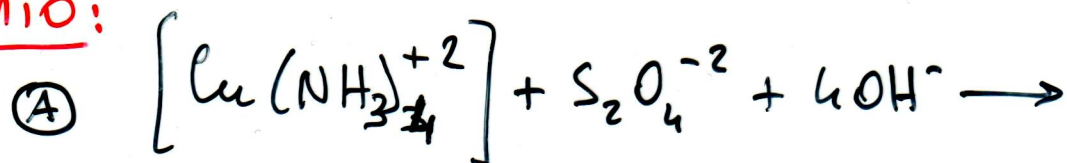
Bismuto:



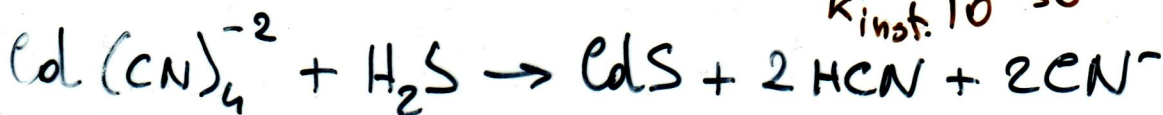
Rame:



Cadmio:



$K_{\text{inst.}} 10^{-30}$

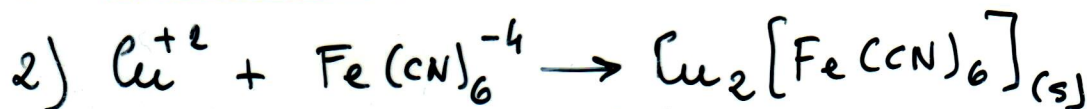
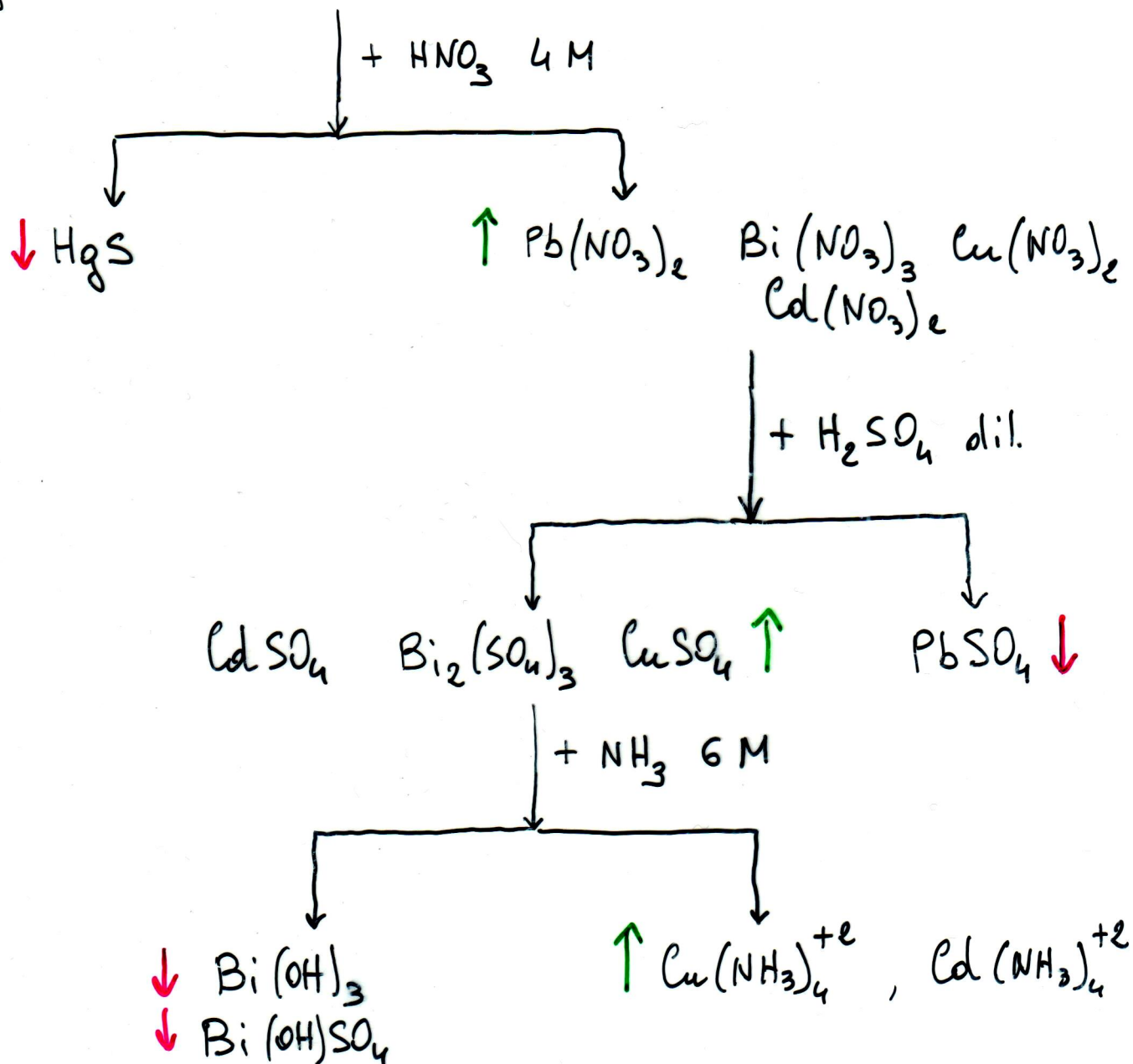


$\hookrightarrow K_{\text{inst.}} 10^{-17}$

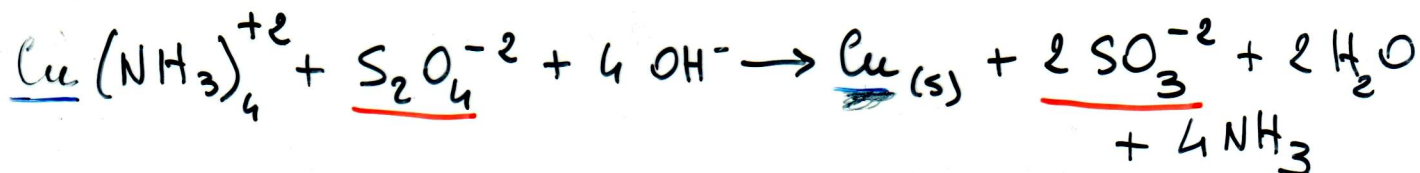
2° GRUPPO

1° Sottogruppo

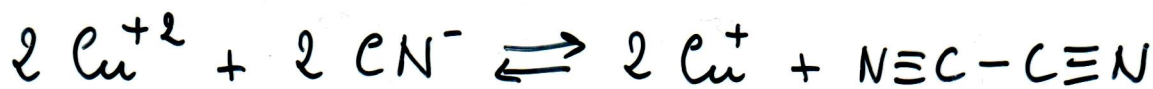
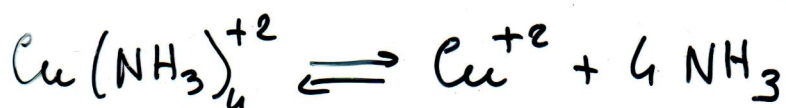
HgS, PbS, Bi₂S₃, CuS, CdS



CADMIO: ① Eliminazione di Cu⁺² con ditionito S₂O₄⁻²



② Mascheramento del Cu^{++} (Cu^+) con CN^-

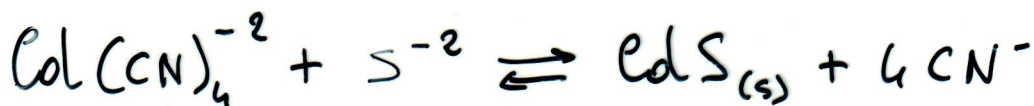


$$\hookrightarrow K_{\text{inst.}} = 10^{-30}$$

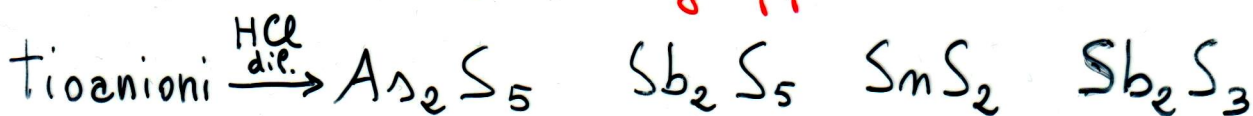


$$\downarrow K_{\text{inst.}} = 10^{-7}$$

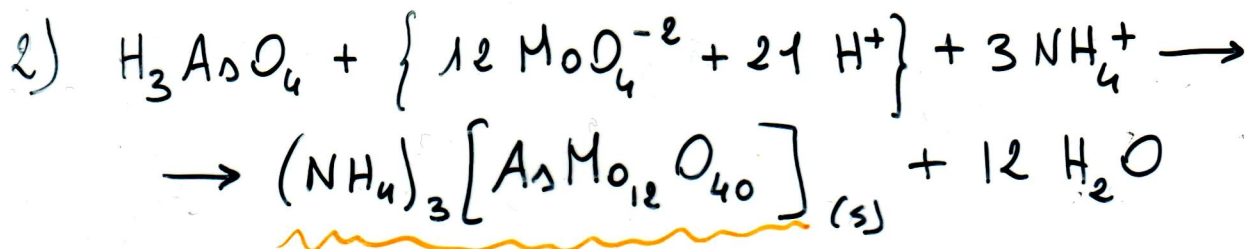
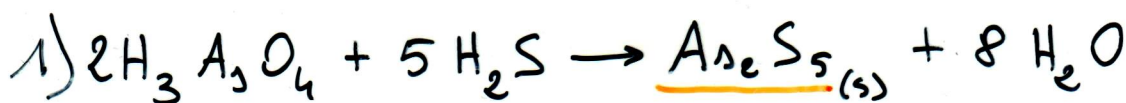
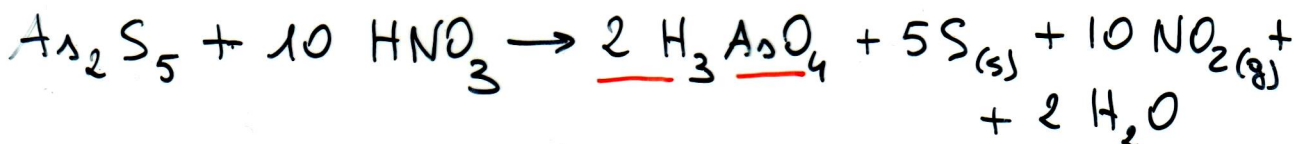
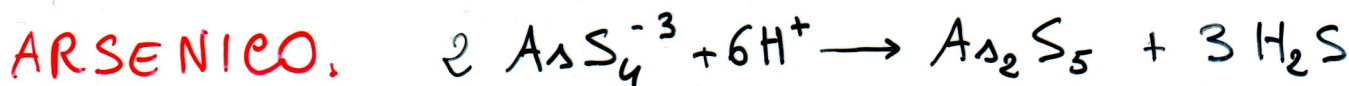
$$\downarrow K_{\text{inst.}} = 10^{-17}$$

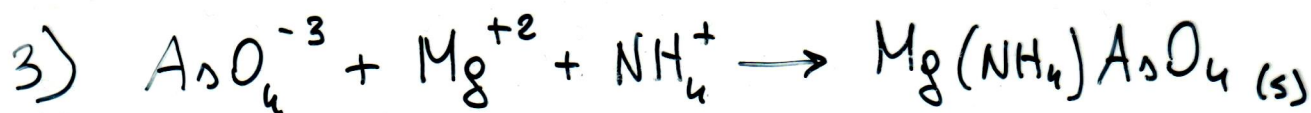


2° Sottogruppo

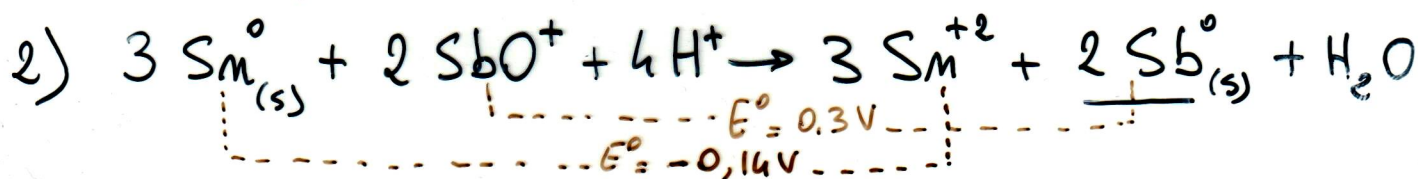
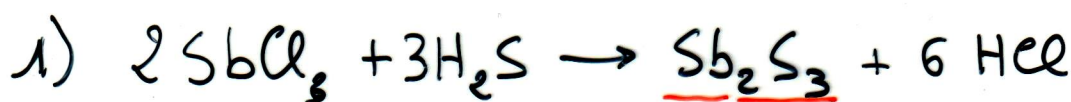
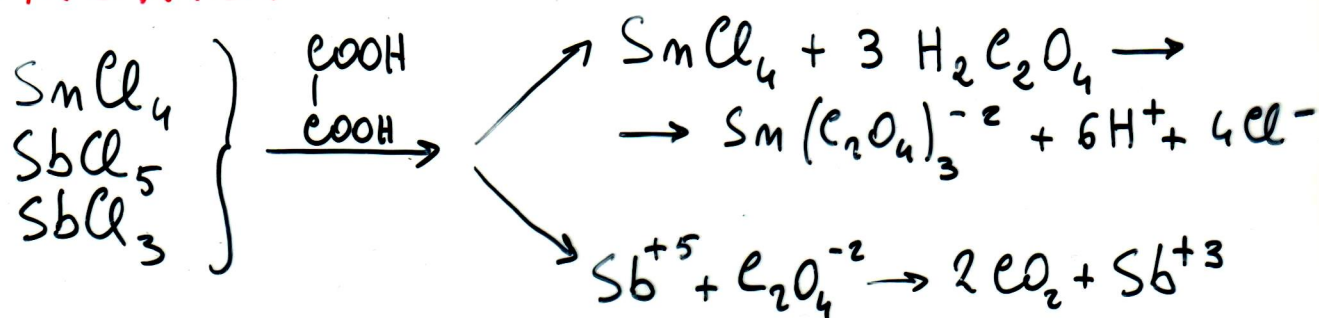


HCl 6 M

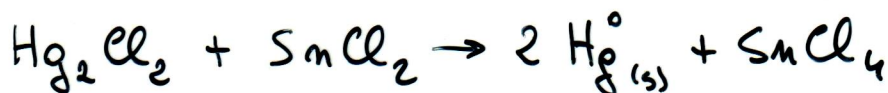
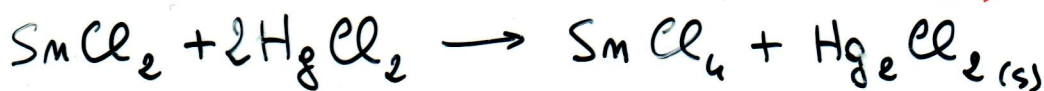
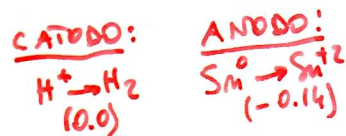
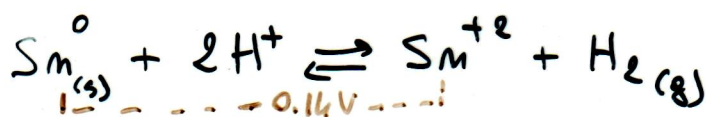
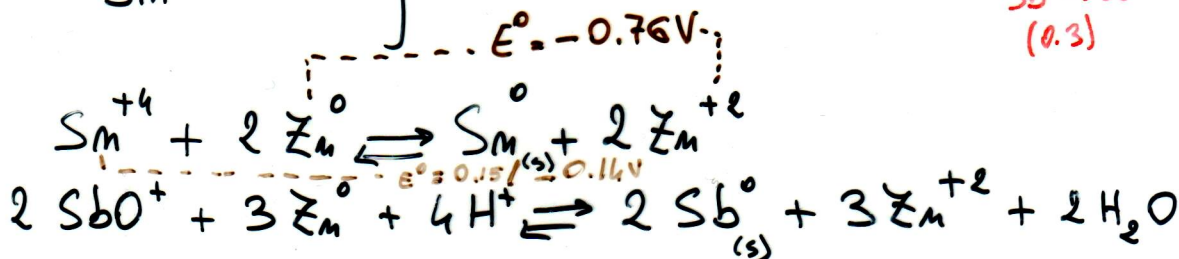
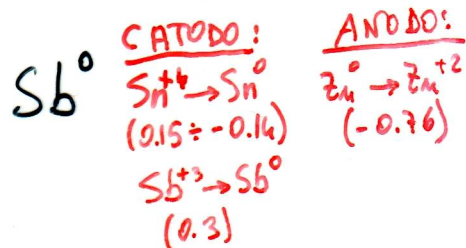
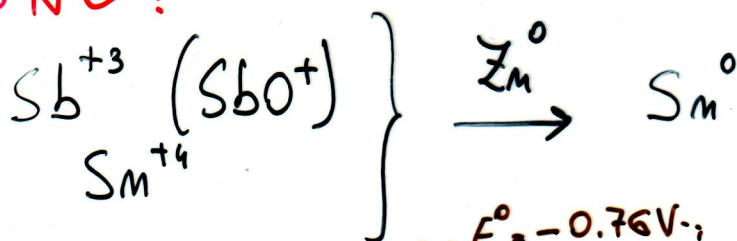




ANTIMONIO:

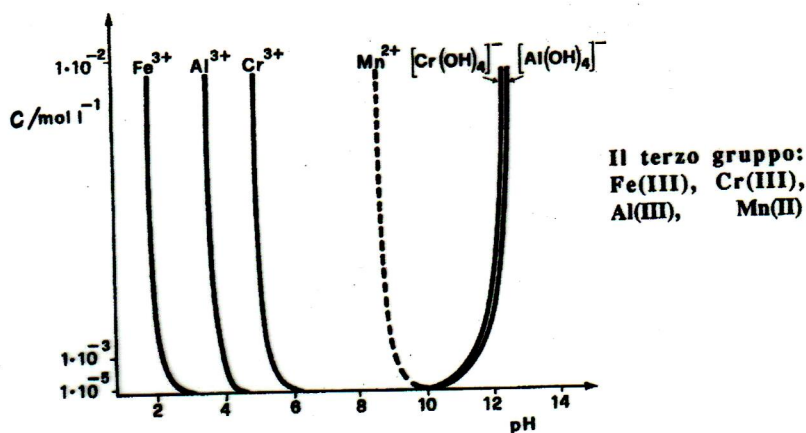


STAGNO:

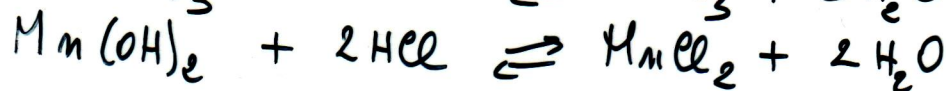
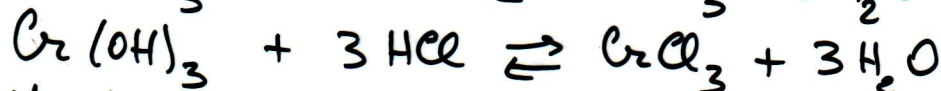
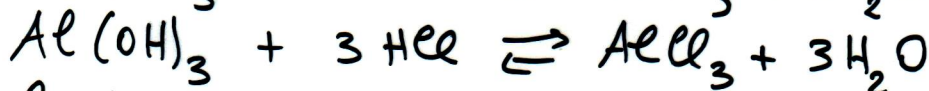
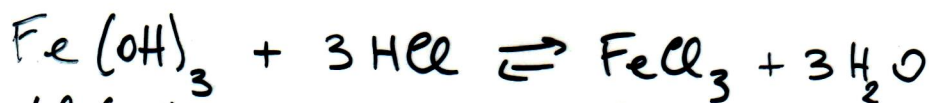
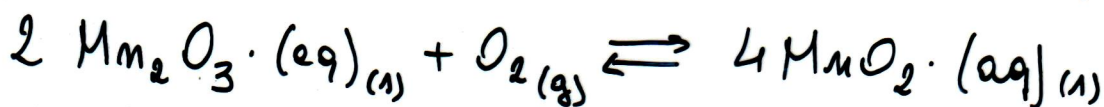
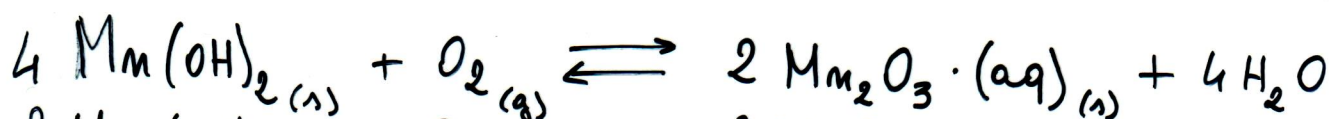
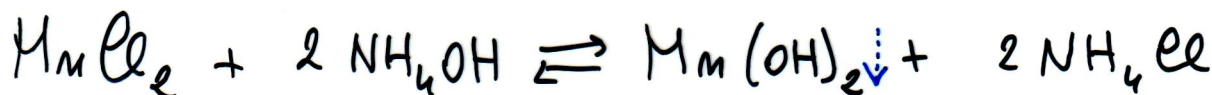
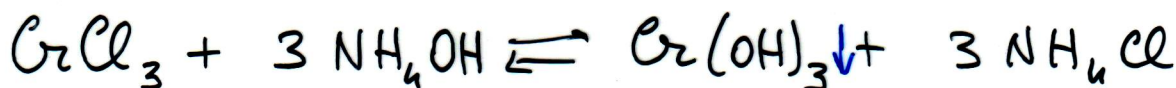
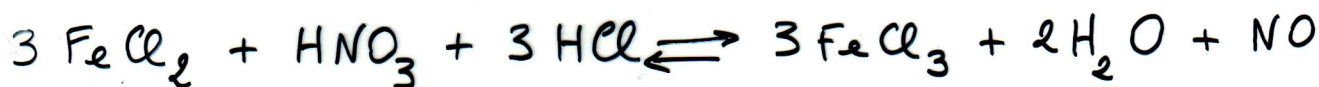


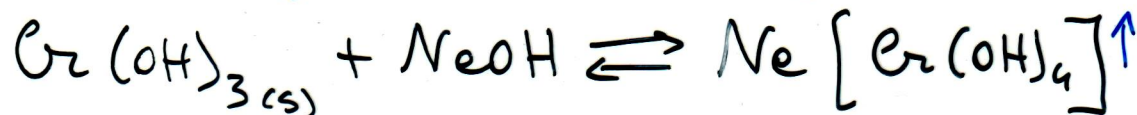
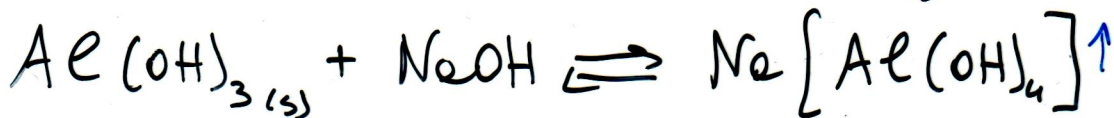
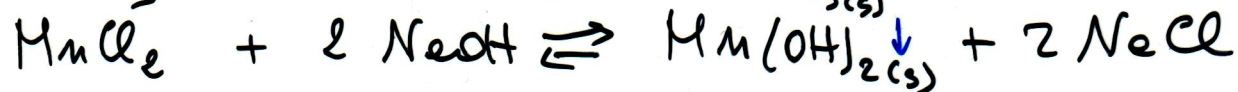
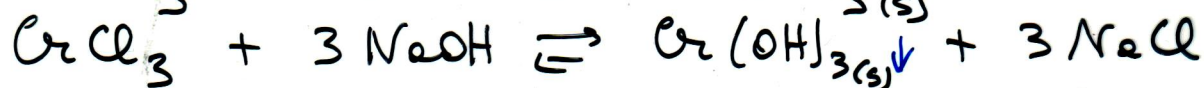
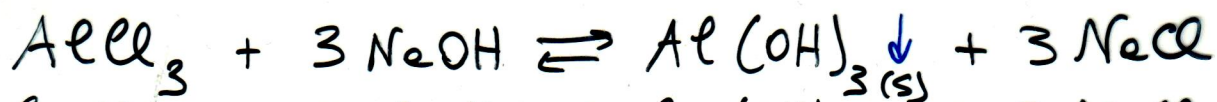
3° GRUPPO

Reattivo precipitante: NH_3 in presenza di NH_4Cl ($\text{pH} = 9$)



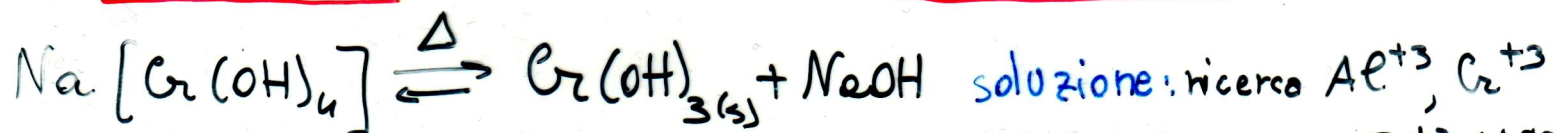
Precipitazione dei cationi del terzo gruppo in funzione del pH





Metodo A

Metodo B



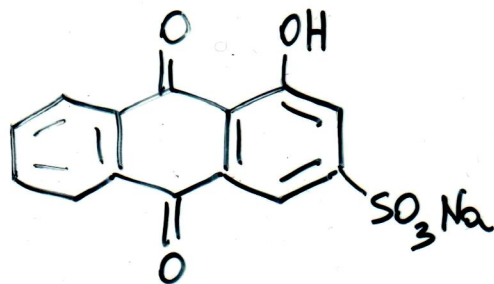
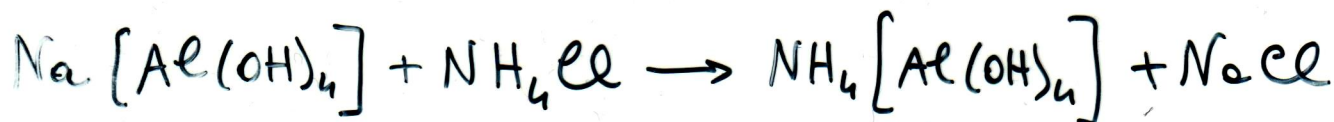
soluzione: ricerca Al^{+3} , Cr^{+3}

precipitato: ricerca Fe^{+3} , Mn^{+2}

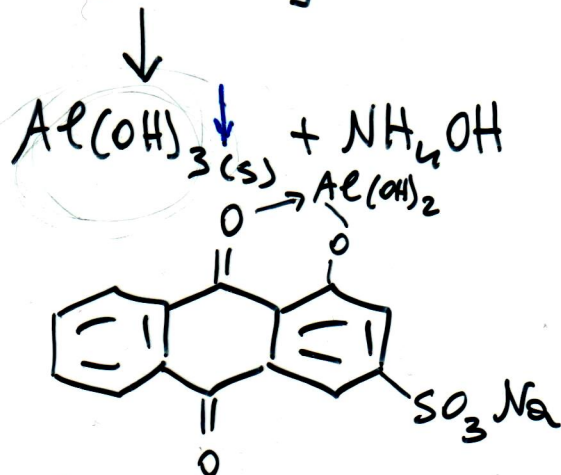
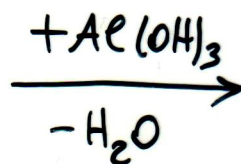
soluzione: ricerca Al^{+3}

precipitato: ricerca Fe^{+3} , Cr^{+3} , Mn^{+2}

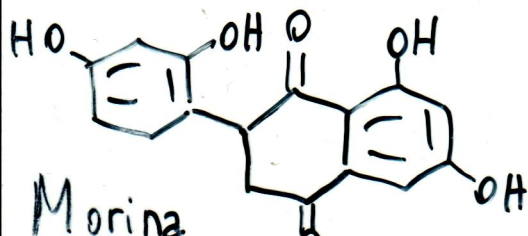
METODO A: Alluminio



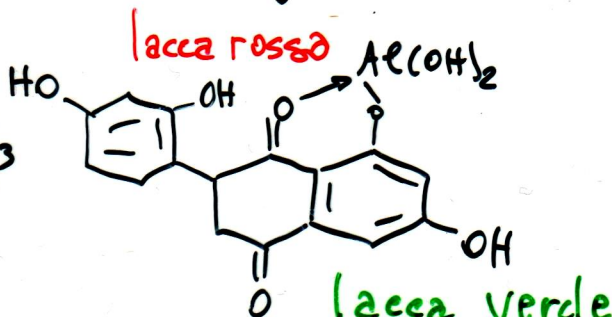
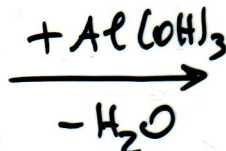
Alizarina S



lacca rosso

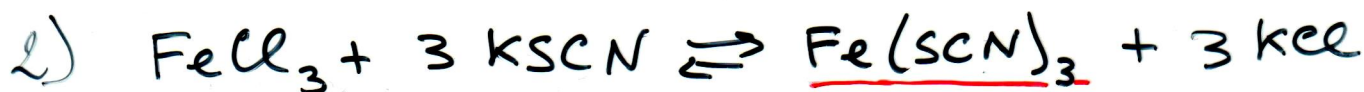
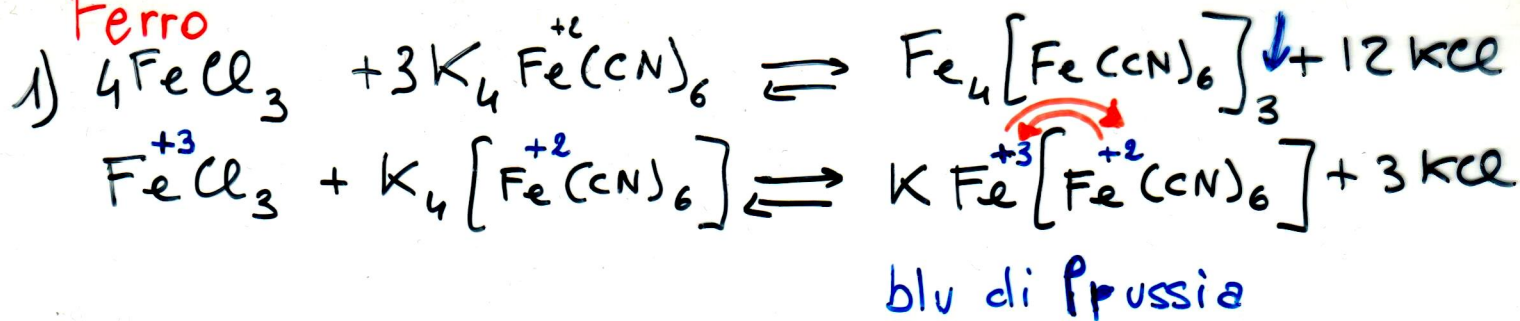


Morina

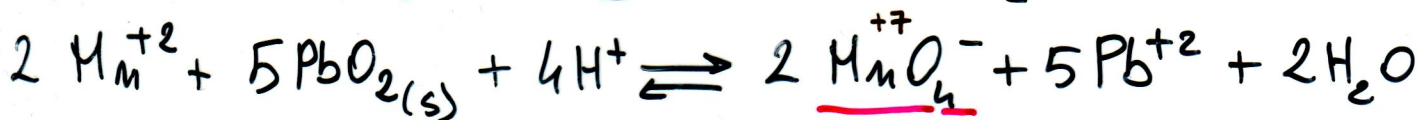
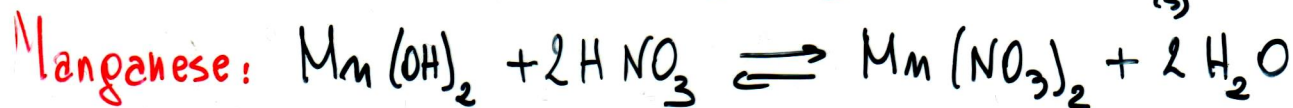
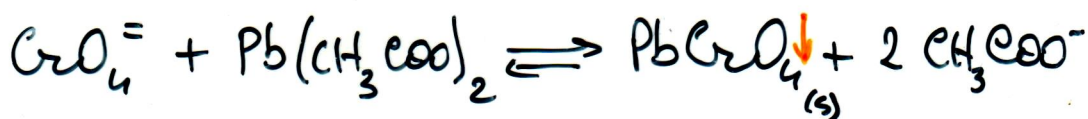
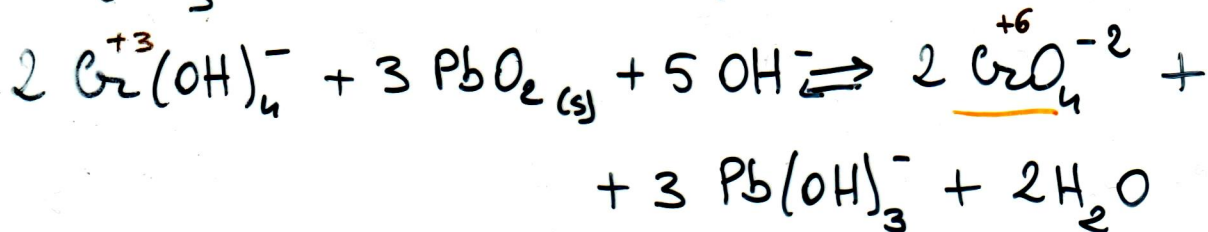
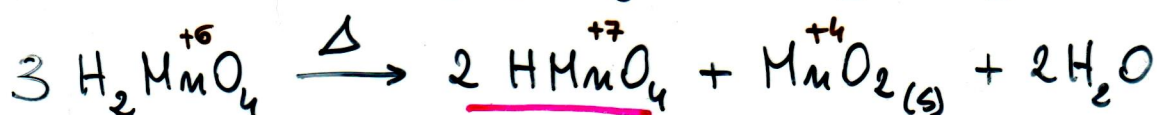
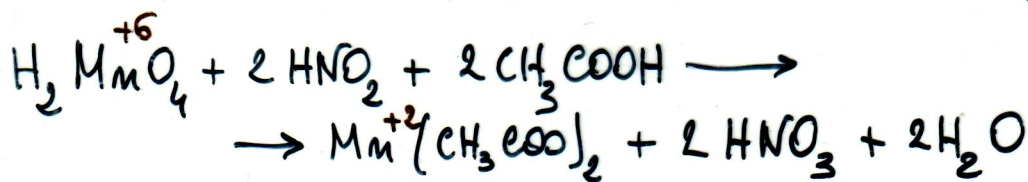
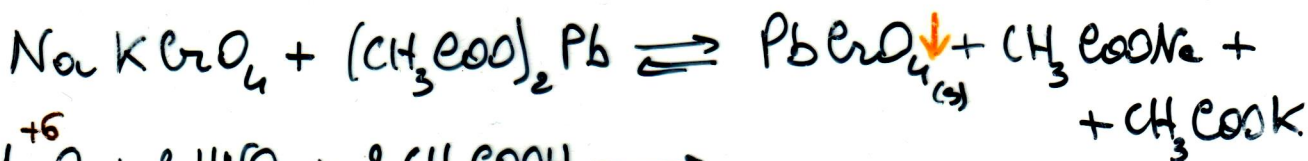
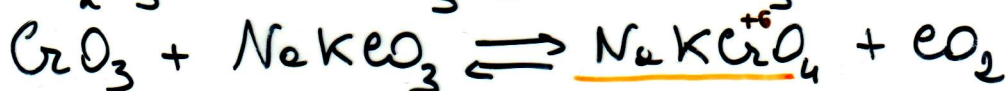
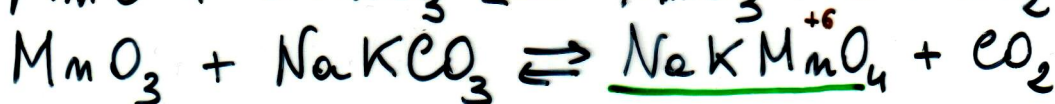


lacca verde

Ferro

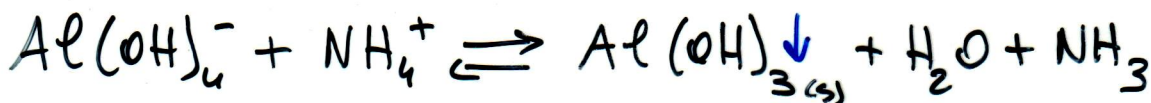
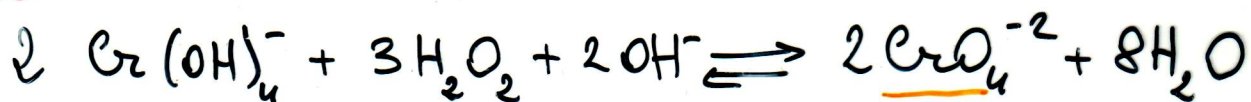


Manganese e Cromo

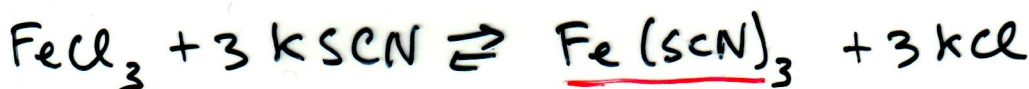


METODO B:

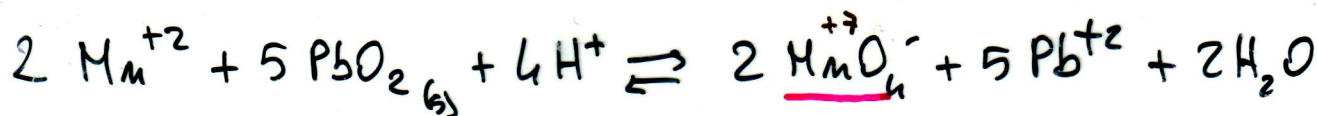
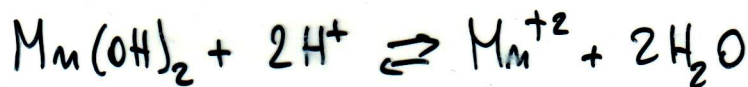
Alluminio



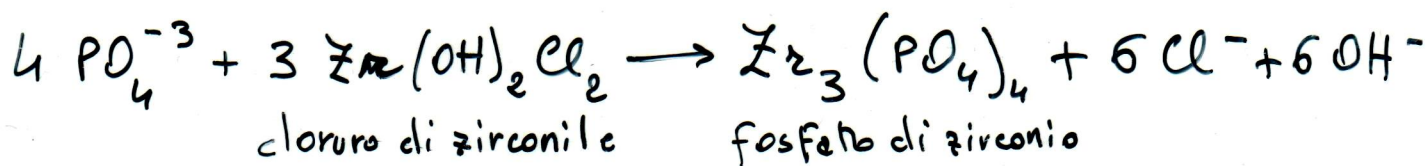
Cromo



Manganese

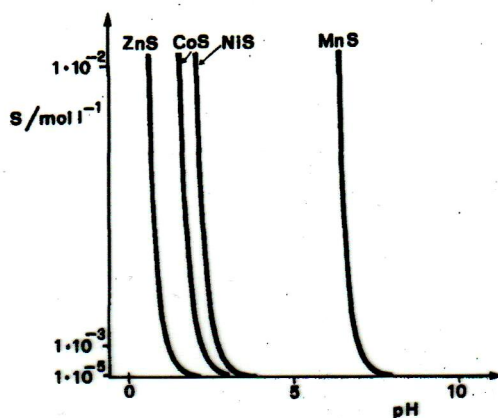


3° GRUPPO COMPLESSO - PRESENZA DI FOSFATI



4° GRUPPO

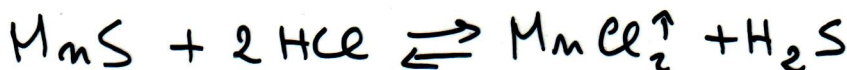
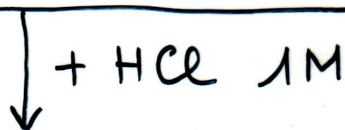
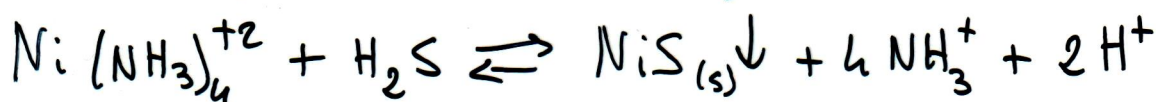
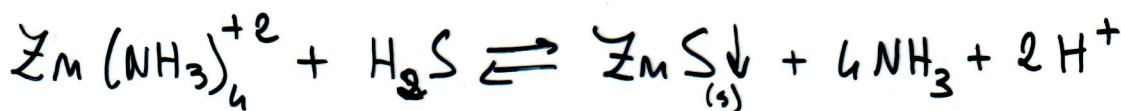
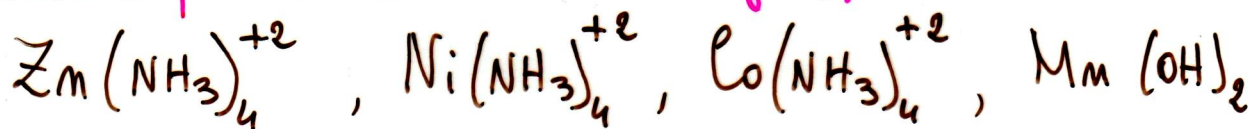
Reattivo precipitante: H_2S (tiosacetammiole) a pH 9.00



Il quarto gruppo:
Ni(II), Co(II),
Zn(II), Mn(II)

Dipendenza dal pH della precipitazione
dei cationi del quarto gruppo da una soluzione
satura di H_2S

Soluzione proveniente dal 3° gruppo:

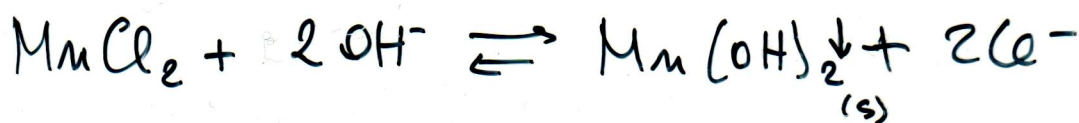


} soluzione

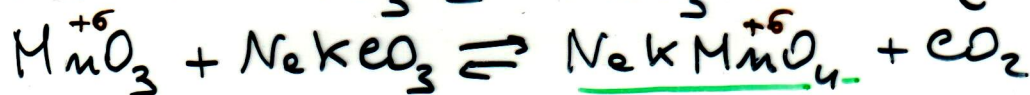
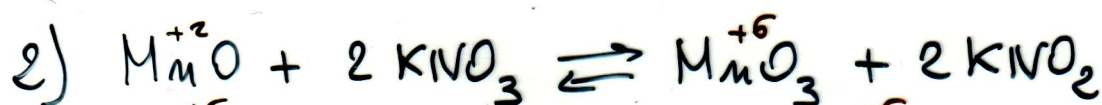
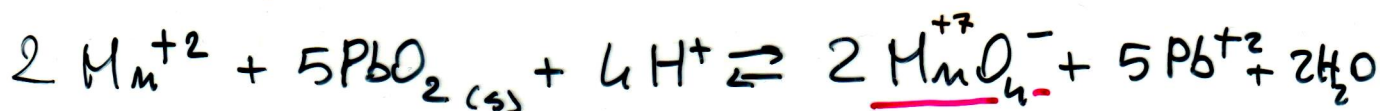
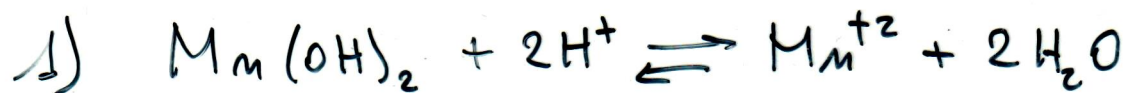


} precipitato

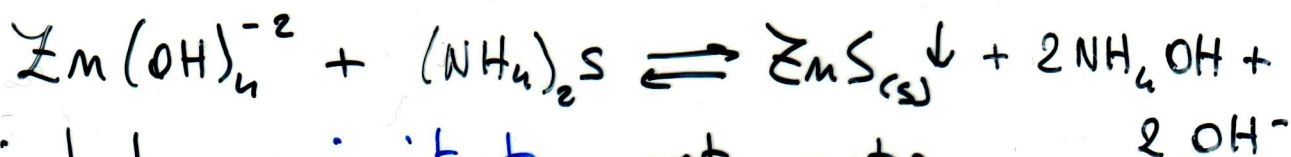
Analisi della soluzione contenente Zn^{+2} e Mn^{+2}



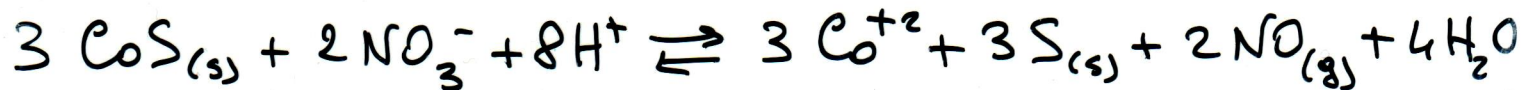
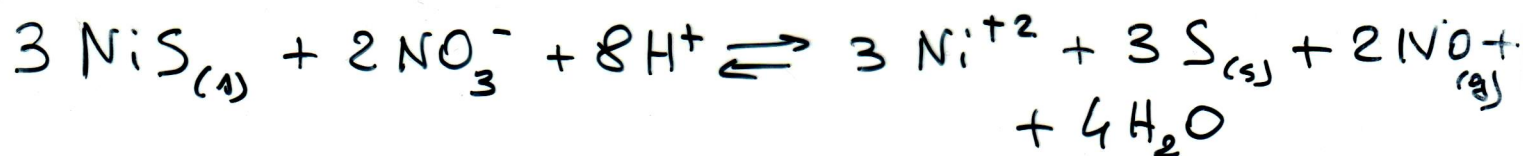
MANGANESE



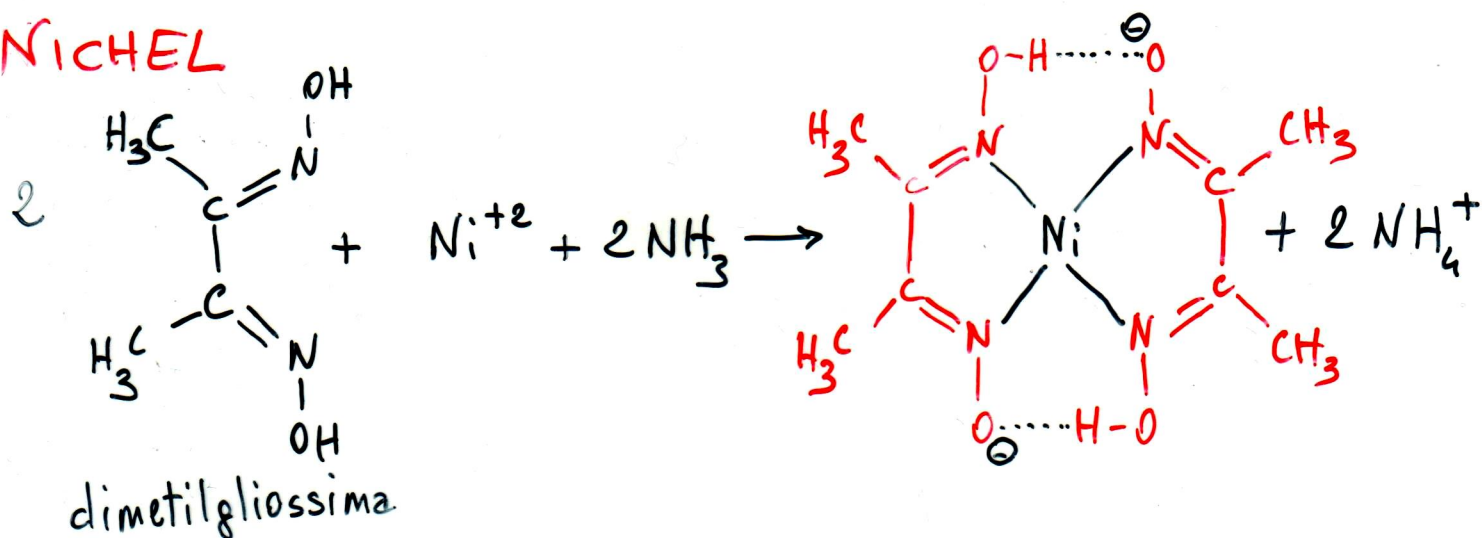
ZINCO



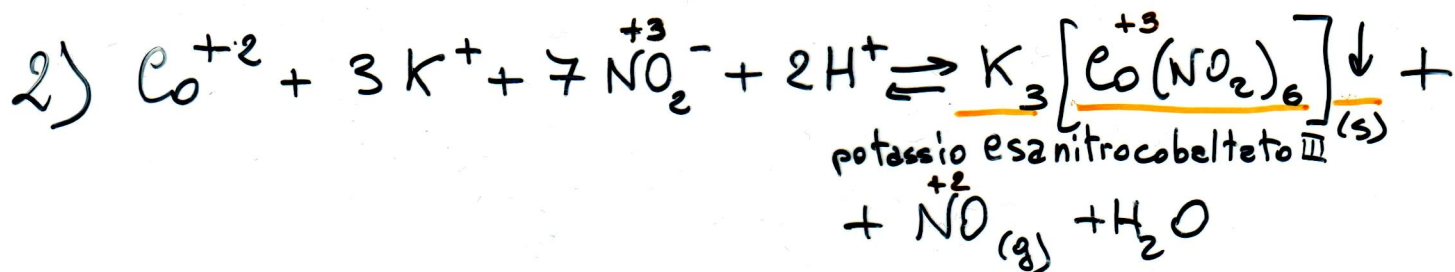
Analisi del precipitato contenente:
 Ni^{+2}, Co^{+2}



NICHEL



COBALTO



ATTIVITÀ FARMACOLOGICA E TOSSICOLOGICA

Manganese Composti di interesse farmaceutico:

KMnO_4 = anti-belt. e disinfezt. uso esterno

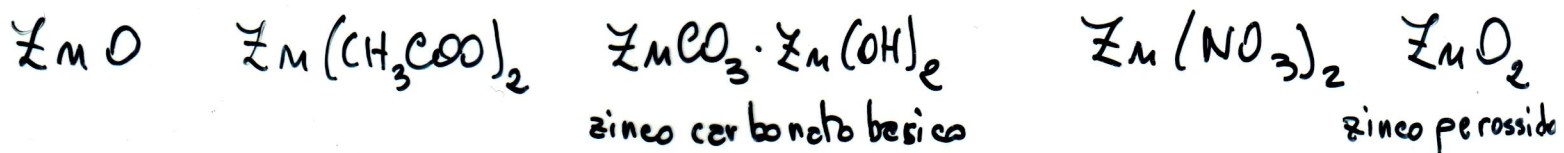
MnSO_4 : reintegratore

AH. farmacologica: entra come cofattore in diversi enzimi:

- isocitrico-deidrogenasi (enzima del ciclo di Krebs)
- Mn-superoossidodismutasi mitocondriale (decomposiz. radicali HO-O^{\cdot} and H_2O_2 e O_2)

Carenza: disturbi crescita e sviluppo corporeo, tremori

Zinco Composti di interesse farmaceutico:



antibatterici, assorbenti, antisettici.

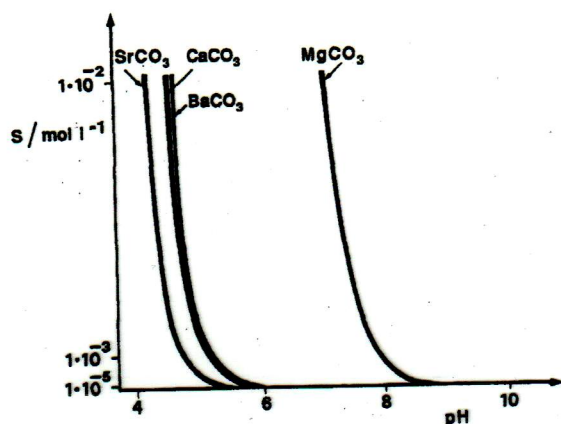
ZnSO_4 = antisettico uso oftalmico; emetico

+ $\text{CuSO}_4 \rightarrow$ antisettico + $\text{K}_2\text{S}_3 \rightarrow$ loz. antiacne

ZnCl_2 = integrante dell'insulina in terapie antidiabetiche.

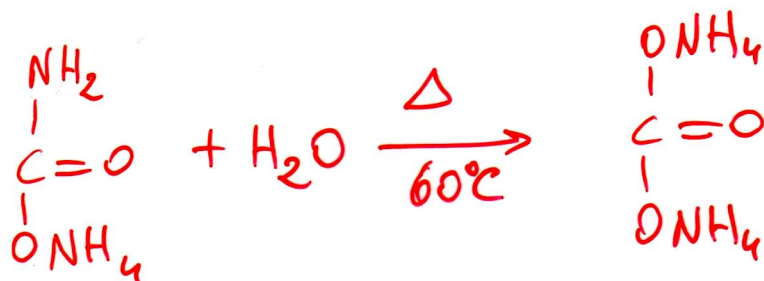
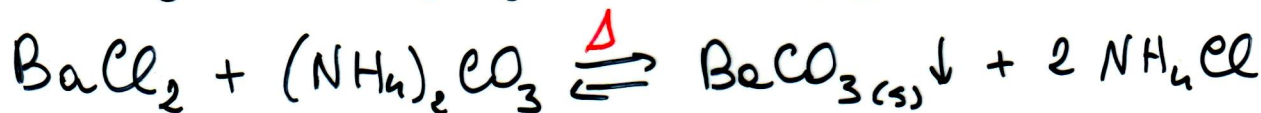
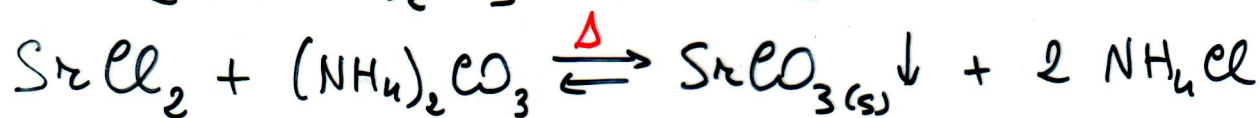
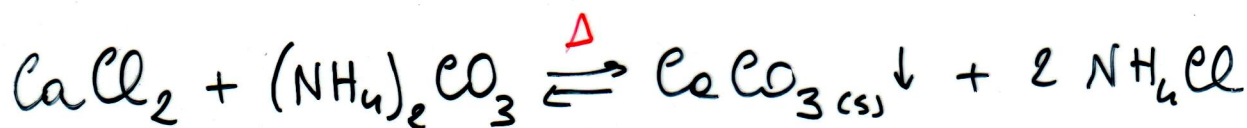
5° GRUPPO

Reattivo precipitante: $(\text{NH}_4)_2\text{CO}_3$ in presenza di NH_3 e NH_4Cl



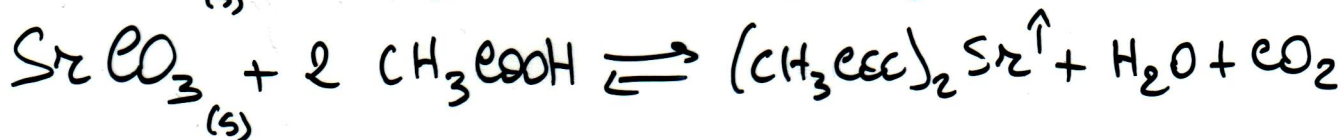
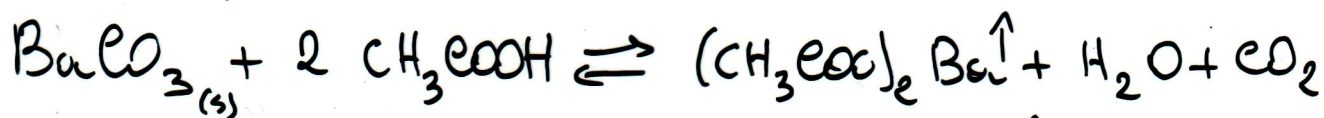
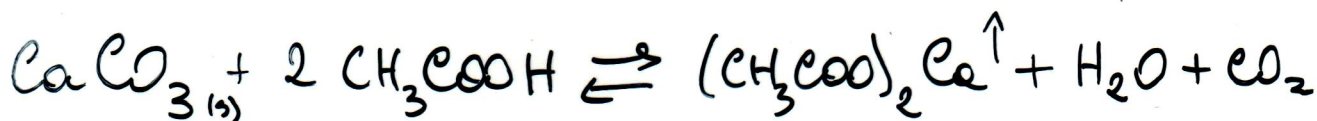
Il quinto gruppo:
 $\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$

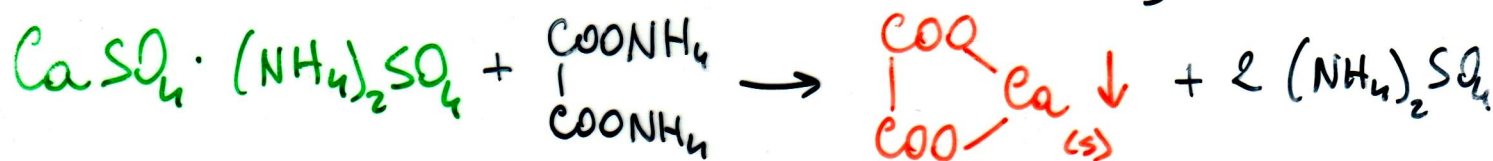
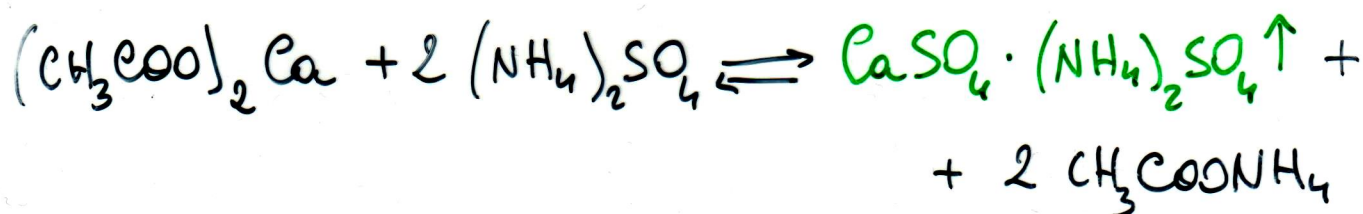
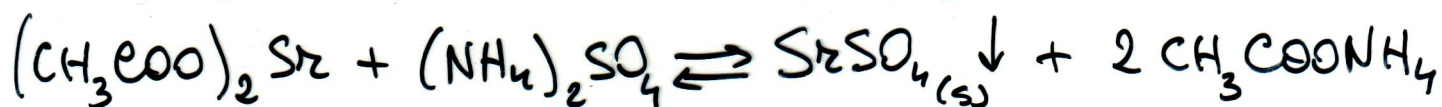
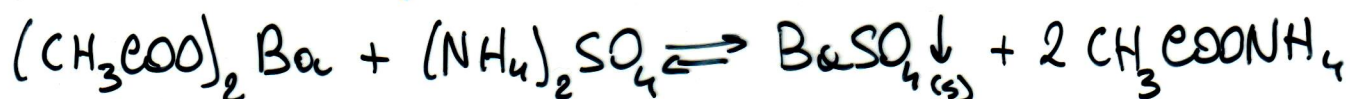
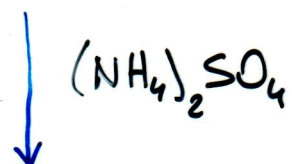
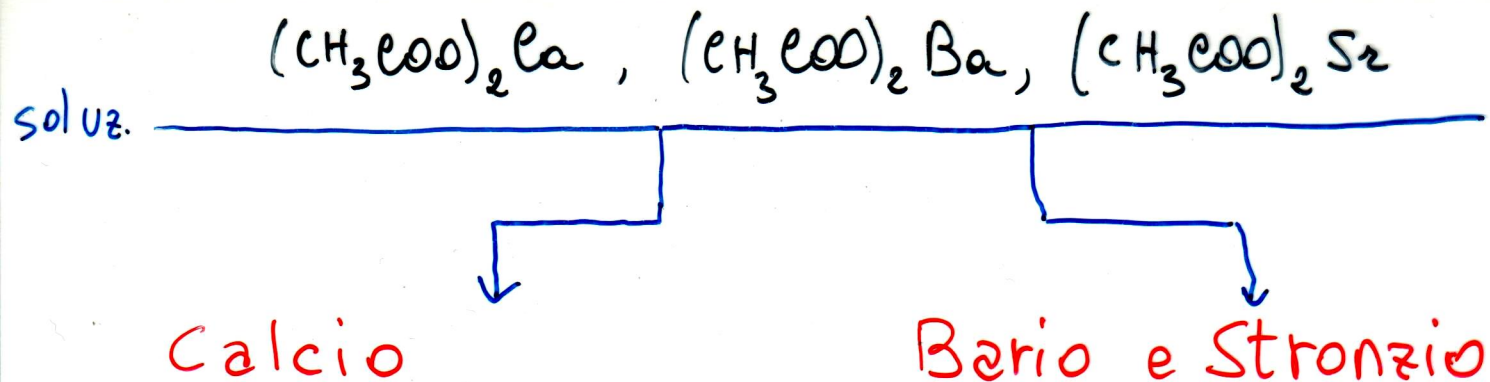
Fig. Precipitazione dei cationi del quinto gruppo da soluzioni 1 M di $(\text{NH}_4)_2\text{CO}_3$ in funzione del pH



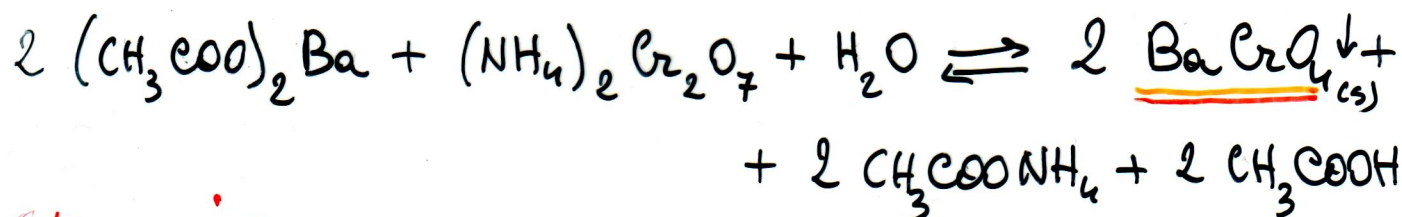
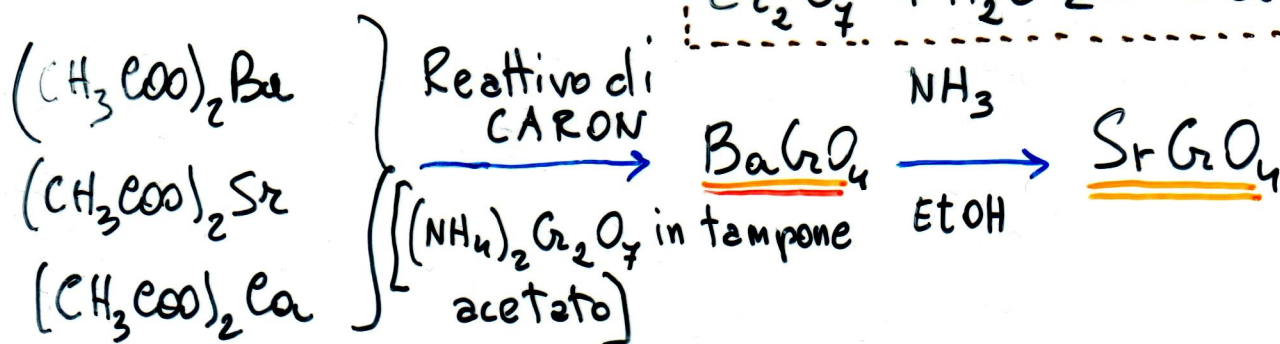
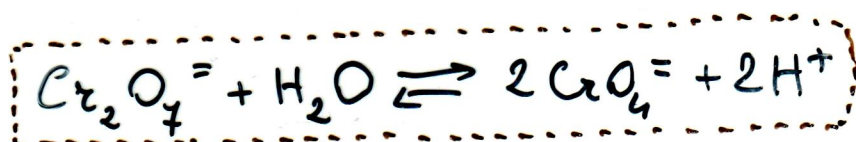
carbammato di ammonio

carbonato di ammonio

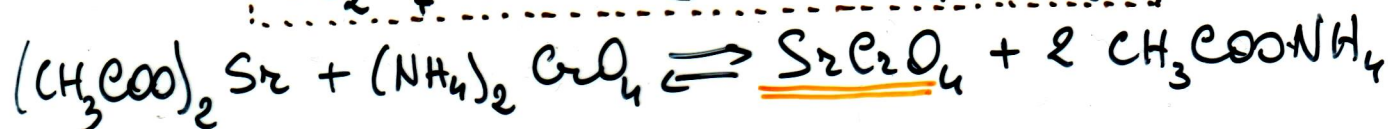
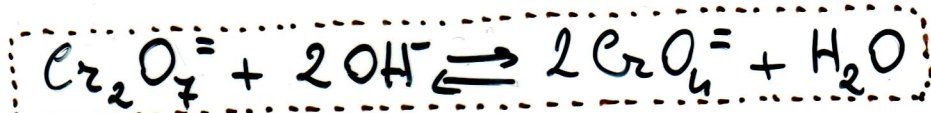




Bario



Stronzio



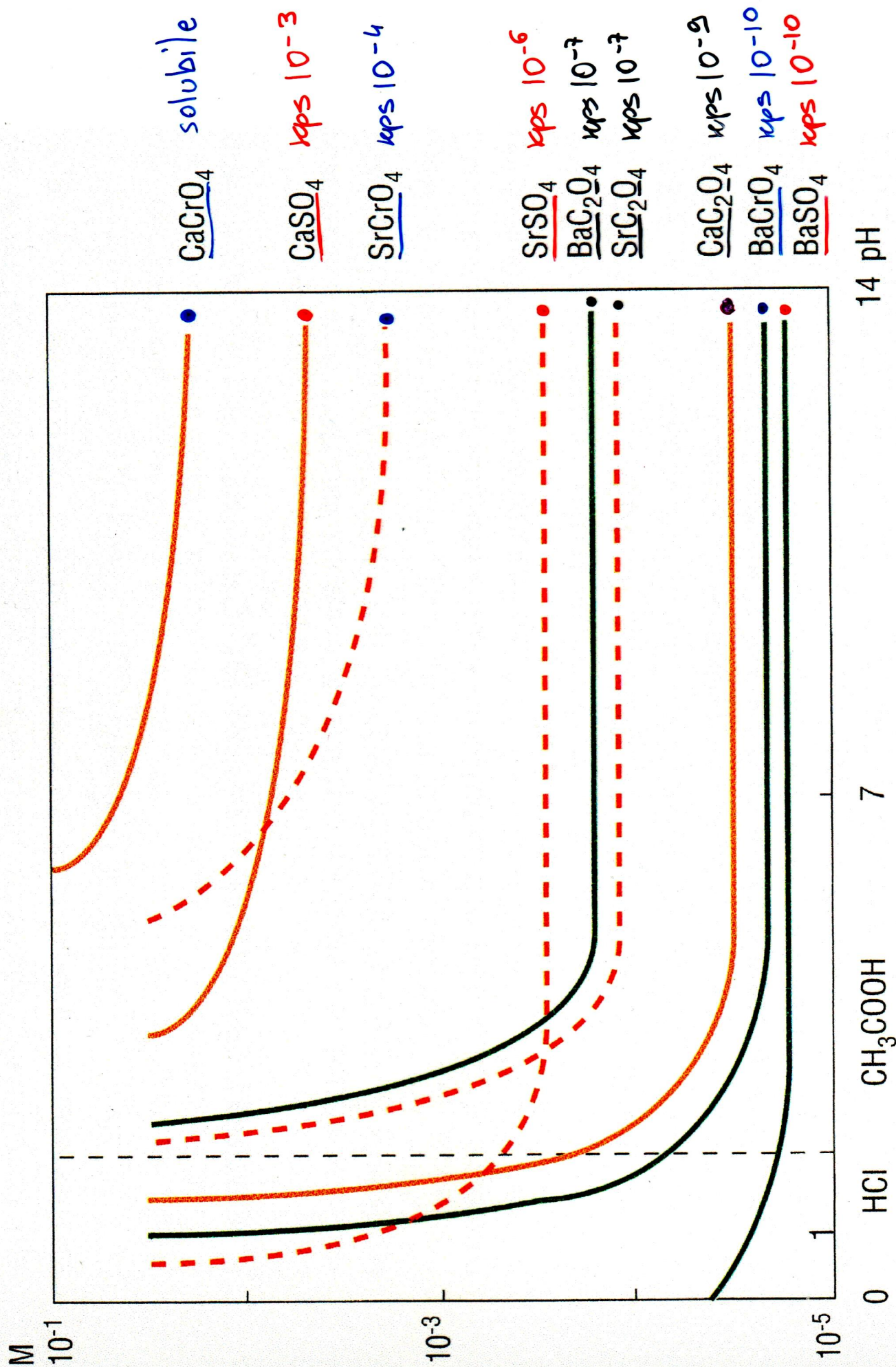


FIGURA 9-3 Solubilità di sali alcalino-terrosi in funzione del pH (valori approssimati).

BARIO Composti di interesse farmaceutico

BaSO_4 = radio-opaco nelle radiografie ai raggi X dell'apparato G.E.

Attività farmacologica e tossicologica

È un catione eliminato simile a Ca^{+2} → ipocalcemia
Avvelenamento: vomito, diarree, crampi muscolari, aritmie, morte per arresto cardiaco
Antidoto: Solfati alcalini

6° GRUPPO

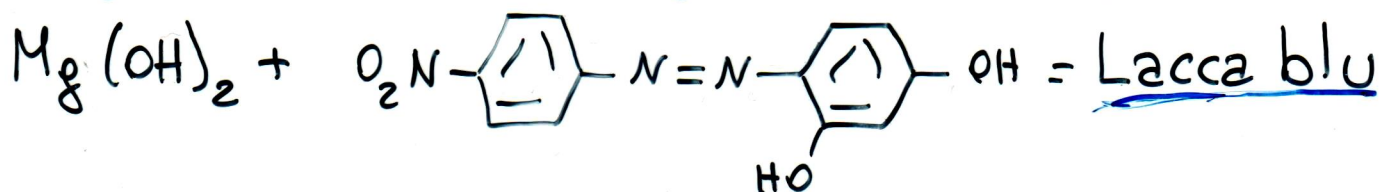
REATTIVO PRECIPITANTE : NESSUNO
CATIONI : Mg, Na, K, Li

Soluz. proveniente dal 5° gruppo } + $(\text{NH}_4)_2\text{SO}_4$ + $(\text{NH}_4)_2\text{C}_2\text{O}_4$

↓
 $\text{BaSO}_4 \downarrow$, $\text{SrSO}_4 \downarrow$, $\text{CaC}_2\text{O}_4 \downarrow$
residui

Sulla soluzione limpida si ricerca anzitutto Mg^{+2}

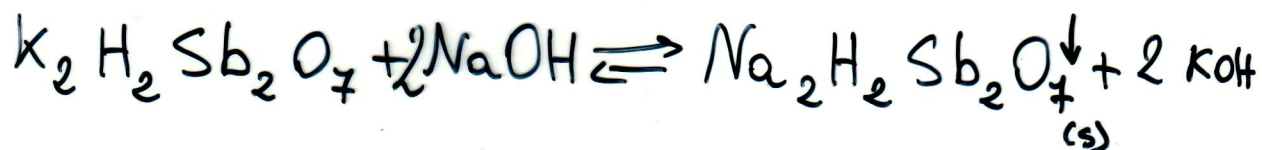
MAGNESIO



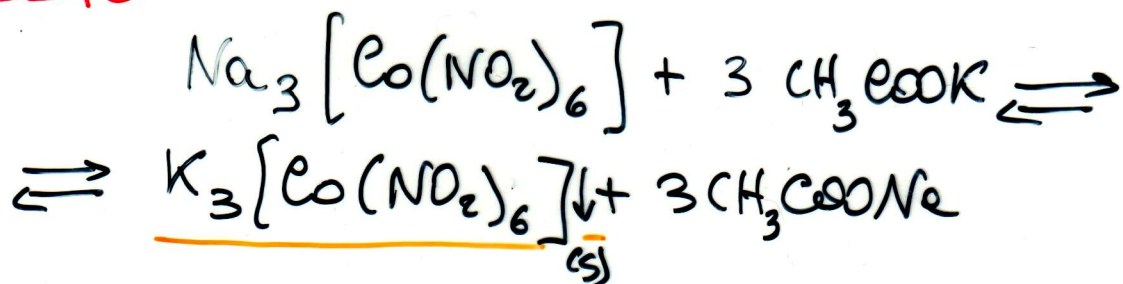


La restante soluzione si evapora su reticella e capsulina fino alla eliminazione dei vapori bianchi di NH_4Cl , quindi si riprende con H_2O e si divide in 2 porzioni (Na - K e Li)

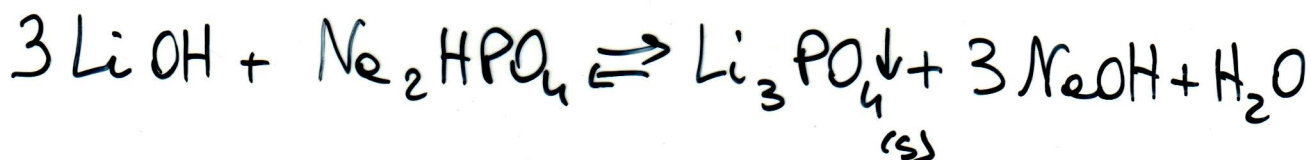
SODIO



POTASSIO



LITIO

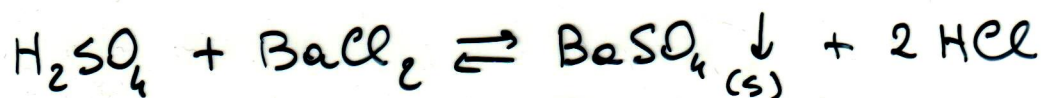


RICERCA DEGLI

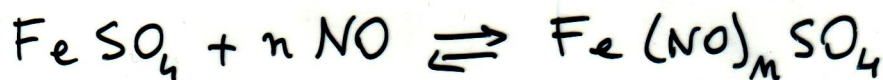
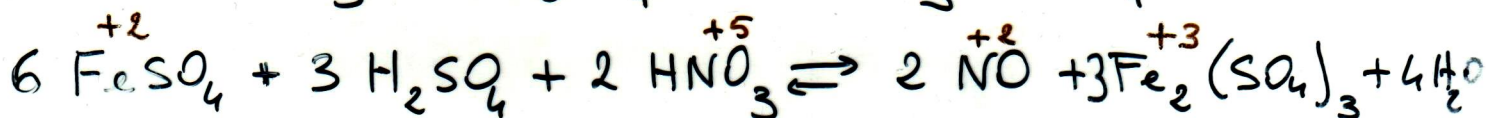
ANIONI

PER VIA UMIDA

SOLFATI

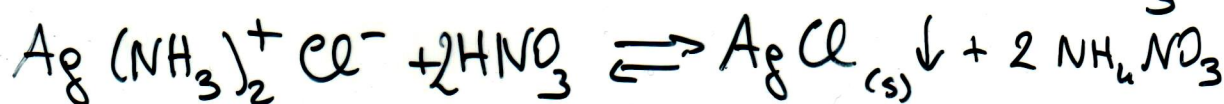
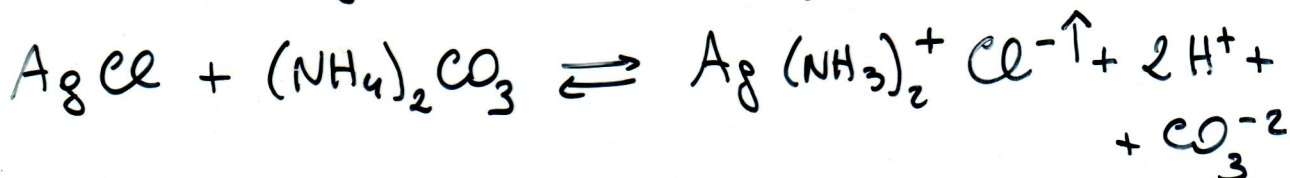


NITRATI

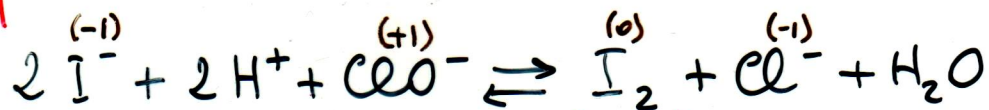


ferro nitrososolfati

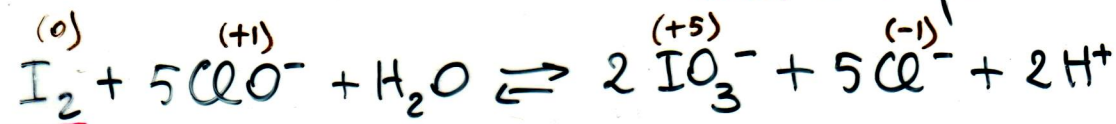
CLORURI



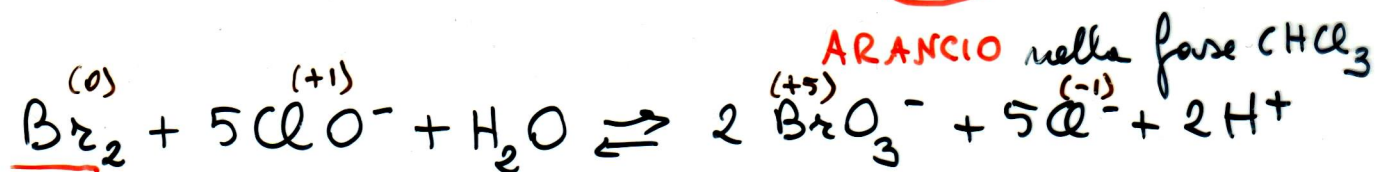
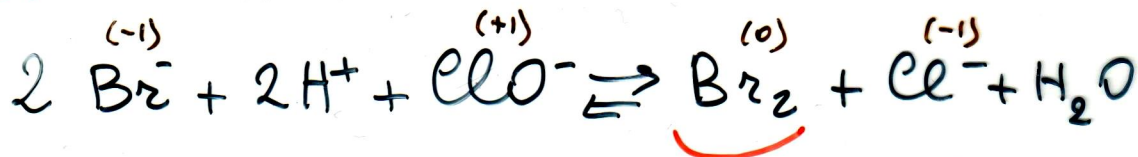
IODURI



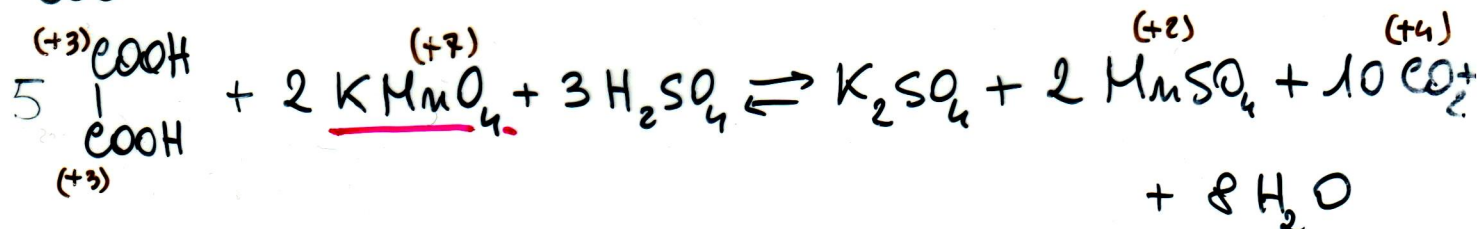
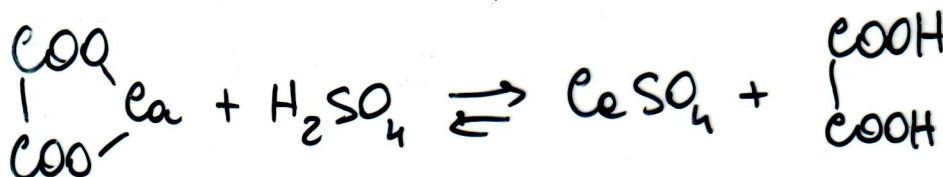
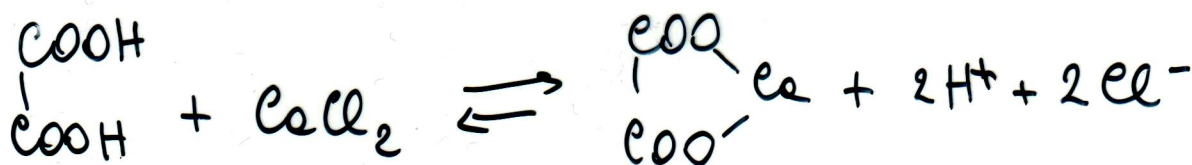
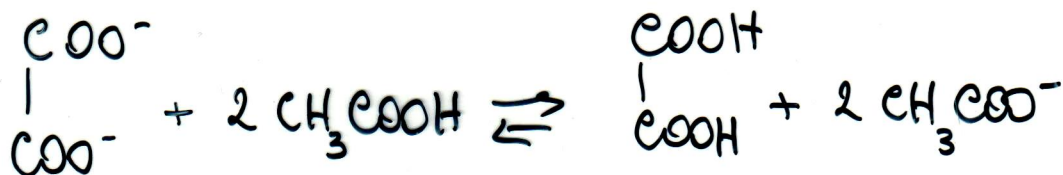
VIOLA nella fase di CHCl_3



BROMURI



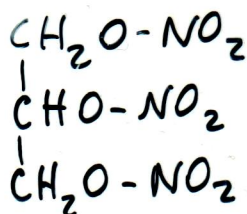
OSSALATI



ATTIVITÀ FARMACOLOGICA E TOSSICOLOGICA

SOLFATI Composti di interesse farmaceutico: Na_2SO_4 , MgSO_4
lunghivi

NITRATI Composti di interesse farmaceutico: NaNO_3 , KNO_3
conservanti in insaccati



nitroglicerina: coronarodilatatore, anti-angina pectoris

Eff. tonici: metemoglobinemia

CLORURI Composti di interesse farmaceutico

HCl NaCl KCl CaCl_2 : reintegratori

NH_4Cl : espettorante, mucolitico

Attività farmacologica: partecipa con ione Na^+ alla regolazione della pressione osmotica di sangue e tessuti ed alla trasmissione dell'impulso nervoso e muscolare ("canali del Cl^- ")

BROMURI Composti di interesse farmaceutico

NaBr KBr CaBr_2 LiBr Mg OHBr NH_4Br
sedativi, antiepilettici

IODURI Composti di interesse farmaceutico

KI NaI = per disfunzioni tiroidee,
 I^{131} : tracciante espettoranti, mucolitici.

Attività Farmacologica e Tossicologica

I^- utilizzato per la sintesi ormoni tiroidei:
tiroxina (T_4) e triiodotironina (T_3)

OSSALATI Tossicologia $\text{C}_2\text{O}_4^{2-}$ è uno ione sequestrante Ca^{+2} , che converte prima in complesso idrosolubile e poi in $\text{C}_2\text{O}_4\text{Ca}_{(s)}\downarrow$, pericoloso sia per la conseguente IPOCALCEMIA che comporta, che per la CALCULOSI RENALE e TROMBOSI VASCOLARE

→ → ALLA SOL. ALCALINA RESULTANTE
SI AGGIUNGE HNO_3 → PRECIPITATO BIANCO
DI AgCl

RICERCA BROMURI E IODURI

2 gocce sol. ALCALINA + H_2SO_4 + 10 gocce
 CHCl_3 + ACQUA DI CLORO (a gocce).
SI AGITA E SI FANNO SEPARARE LE FASI.
IN PRESENZA DI IODURI IL CLOROFOR-
MIO APPARIRÀ VIOLETO.

SI AGGIUNGE ANCORA ACQUA DI CLORO
GOCCIA A GOCCIA E SI AGITA.

IN PRESENZA DI BROMURI IL CLORO-
FORMIO APPARIRÀ ARANCIONE
E CON ECCESSO DI ACQUA DI CLORO

→ GIALLO PALLIDO

RICERCA OSSALATI

4-5 gocce sol. ALCALINA + CH_3COOH
SI ELIMINA CO_2 .

→ →

RICERCA NITRATI

SOL. ALCALINA + H_2SO_4 dil + 1 PUNTINA
DI SPATOLA DI $FeSO_4 \rightarrow$ SOL. SATURA
SI AGGIUNGE CON PIPETTA 0.2-0.3 ml
DI H_2SO_4 CONC. FACENDOLO SCORRERE
SULLE PARETI.

L' H_2SO_4 CONC. SI STRATIFICA SUL FONDO
SENZA MESCOGLIARSI ALLA SOLUZ.
IN PRESENZA DI NITRATI SI FORMA
UN ANELLO BRUNO ALL' INTERFAC.
CIA DOVUTO ALLA FORMAZIONE DI
 $Fe(NO)_3SO_4$.

N.B. LA REAZIONE E' POSITIVA ANCHE
X IODURI, BROMURI E NITRITI

RICERCA CLORURI

5 gocce SOL. ALCALINA + HNO_3 + $AgNO_3$
ECESSO
SI CENTRIFUGA E SI LAVA IL PRECIPITATO.
AD ESSO SI AGGIUNGE UNA SOL. DI
 $(NH_4)_2CO_3$ E SI CENTRIFUGA \rightarrow

RICERCA DEGLI ANIONI

PREPARAZIONE DELLA SOLUZIONE ALCALINA

100 - 150 mg SOSTANZA + 0.3 - 0.5 g Na_2CO_3 + 5-10 ml H_2O

SI FA BOLLIRE x 30', SI RAFFREDDA E SI CENTRIFUGA.

IL LIQUIDO SOVRASTANTE RAPPRESENTA LA SOLUZIONE ALCALINA CHE CONTIENE GLI ANIONI SOTTO FORMA DI SALI SODI. CI.

RICERCA DEI SOLFATI

4-5 gocce DI SOL. ALCALINA + HCl dil
SI RISCALDA x ELIMINARE CO_2 E SI AGGIUNGE $\text{BaCl}_2 \rightarrow$ PRECIPITATO BIANCO
CHE PERMANE DOPO AGGIUNTA DI 2-3
GOCCE DI HCl conc.

→→→ SI AGGIUNGONO POCHÉ GOCCE
DI SODIO ACETATO + 3-4 gocce di
 $\text{CaCl}_2(\text{sol})$.

SI RISCALDA X ALCUNI MIN A BAGNO-
MARIA → PRECIPITATO BIANCO DI
OSSALATO DI CALCIO

SI CENTRIFUGA E SI LAVA IL RESIDUO
CON H_2O . IL SOLIDO SI SCIoglie CON
4-5 gocce di H_2SO_4 dil (2N) E
SI AGGIUNGE UNA GOCCE DI KMnO_4
dil (0.05 N) E SI SCALDA A
50-60°C.

IN PRESENZA DI AC. OSSALICO
LA SOL. SI DECOLORA (PASSA DA
VIOLETTO A INCOLORE)